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LIQUID PHASE EQUILIBRIA IN THREE-COMPONENT

SYSTEMS

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A large number of studies have already been made of the problem of liquid phase equilibria in three-component systems in which two or three binary layers are formed. The results obtained may be summed up in the diagrams below (Fig. 1, a and b).

Fig. 1.

When two binary layer formations occur in the boundary systems AC and BC, the ternary system is found to contain either t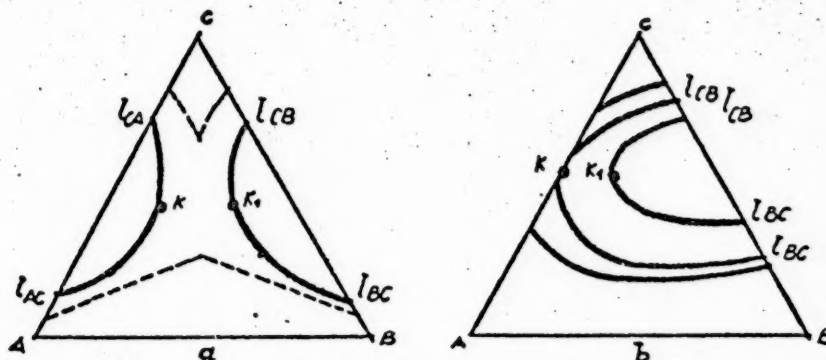wo separately existing regions of layer formation with the independent critical point K and K_1 (Fig. 1, a) or a single region of layer formation extending from the one binary system, for example BC (Fig. 1, b), to the other one (AC); the critical point of the region of layer formation (K_1) with a binodal curve in the ternary system merges with the critical point (K) of binary layer formation on approach to the binary system AC. In the first of the cases considered, with decreasing temperature the regions of layer formation may merge with each other to form a single region of layer formation with a node thereon (broken lines in Fig. 1, a). Both cases were investigated by Schreinemakers with reference to the systems succinonitrile – water – ethyl alcohol [1] and aniline – phenol – water [2]. Merging of the two regions of layer formation was found in the systems acetic anhydride – water – gasoline [3] and acetic anhydride – water – carbon bisulfide [4]. Formation of three liquid phases is observed in many systems with three binary layer formations; as far as can be judged by previous experiment the temperature of development of this state in the ternary system is higher than one or even two of the critical temperatures of layer formation of binary systems. This holds good for

the systems aniline – water – isooctane, phenol – water – isooctane, and anil-
ine – water – heptane (among others), and permits the conclusion that formation
of a field of three liquid phases is not connected with the mutual intersection
of the three fields of layer formation proceeding from the sides of the systems
undergoing binary layer formation. It occurs as the result of intersection of
the binodal curve, developed from one of the binary enclosed systems, with the
labile field of layer formation enclosed in the latter. On the left hand side
(a) of Fig. 2 is represented the moment when the labile region of layer formation
(broken curve) with its critical point K_1 lies on the stable binodal curve
$l_{AC}K_{l_{AC}}$, with formation of the critical node K_1l. Emerging beyond the stable
binodal curve, the labile binodal curve also, in part, becomes stable, as repre-
sented by $l_1K_1l_2$ (Fig. 2, b). Simultaneously a field of a three-phase liquid
state, ll_1l_2, is developed. With further change of temperature, the binodal
curves $l_1K_1l_2$ and lKl_2 are shifted in the direction of the lines of the binary
systems AB and BC. It is necessary to clarify the subsequent change in the
equilibrium pictures and at the same time to establish a consistent viewpoint
permitting the correlation of all of the facts so far known relating to the
mutual behavior of the various regions of layer formation. On such a basis it
should be possible to predict the existence of other relations.

Such a generalized viewpoint may be developed on the following lines. We
shall assume that each layer formation of a binary enclosed system inside a ter-
nary system always involves an independent region of layer formation which may
be either entirely stable or partly stable, or, again, completely labile. The
last two possibilities naturally arise when two regions of layer formation
intersect.

We shall show that this assumption can serve as a basis of correlation of
all of the known pictures of layer formation of ternary systems. In Fig. 1, a,
is represented the liquid phase equilibrium in a ternary system in which layer
formation takes place in two enclosed binary systems AC and BC. In full agree-
ment with the foregoing postulate, the ternary system contains two binodal curves
$l_{AC}K_{l_{CA}}$ and $l_{BC}K_{1}l_{CB}$. If they mutually intersect (broken curve in Fig. 1, a), a
portion of each region of layer formation becomes labile and no longer exists in
practice. Let us now assume that with change of temperature one of the regions
of layer formation is enlarged within the composition triangle to a greater ex-
tent than the other. Then as can readily be understood, the imaginary portion
of the second region of layer formation will increase in size and simultaneously
the place of mutual intersection of the regions is bound to be shifted in the
direction of this binary boundary system. These changes are illustrated in Fig.
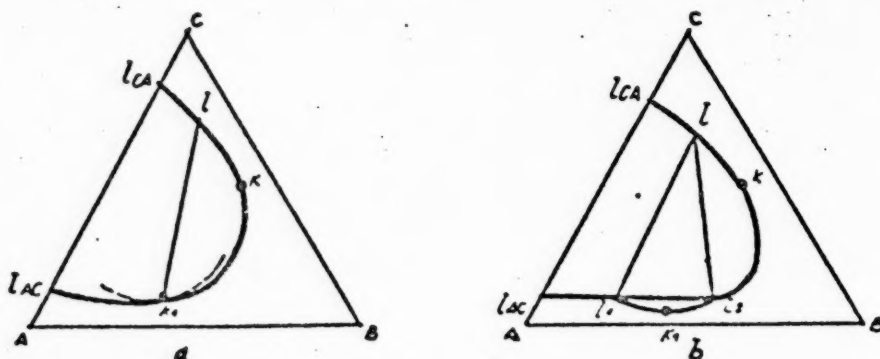3. The left hand portion a represents the intersection of two regions $l_{AC}K_1l_{CA}$

Fig. 2.

and $l_{CB}K_1l_{BC}$ at the point l and l_1 with formation of two imaginary binodal portions l_1Kl and $l_:K_1l$. The same equilibrium is shown in Fig. 3, b, but under different temperature conditions. Whereas the binodal curve $l_{AC}K_1l_{CA}$ barely penetrates into the composition triangle, the binodal curve $l_{CB}K_1l_{BC}$ now has its critical point K considerably closer to the line of the binary system AC. At the same time the points of intersection l and l_1 of the binodal curves will
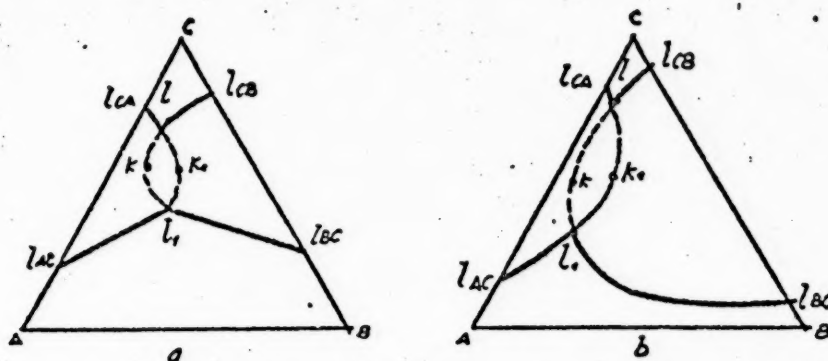

Fig. 3.

also be closer to that line. The very fact that the fictitious critical point K comes close to the line of the binary system AC is evidence of the

possibility of labile layer formation therein; this layer formation also occurs at the temperature at which the point K lies on the line AC inside the segment $l_{AC}l_{CA}$. Starting from this temperature, the labile portion l_1Kl of the birodal curve $l_{BC}Kl_{CB}$ will cut the line $l_{AC}l_{CA}$ at two points corresponding to the mutually saturated solution of labile layer formation in the binary system AC. In this connection points l and l_1 are bound to approach closer and closer to the points l_{CA} and l_{AC} respectively and to merge with them when a temperature is reached at which labile layer formation in the binary system AC disappears. A case of this type was found experimentally by R.V.Mertslin in the system water — phenol — ammonium thiocyanate [5]. It may happen that the region of layer formation $l_{CB}Kl_{BC}$ will reach the line of the binary system AC not at its labile critical point but at the stable point. In that event, with change of temperature the points of intersection l and l_1 of the two regions of layer formation will invariably lie on the line AC corresponding to the composition of the equilibrium liquid phases of this binary system; on penetrating, however, into the composition triangle the region of layer formation will remain fully labile. Evidently in this case we have the equilibrium picture observed by Schreinemakers in the system aniline — phenol — water.

If we apply the foregoing considerations to the case of formation of three liquid phases, we may anticipate the formation of diverse diagrams of state depending upon whether stable liquid two-phase equilibria are set up from each of the binary systems AB and BC, or whether both of these equilibria will be labile. Another possibility is that one of them will have a stable and the other a labile character. Finally, the possible variations will increase considerably if, with change of temperature, we take into consideration the possiblity of interchange of one stable phase with another.

In Fig. 4 are represented the isotherms of one of the possible cases with progressive fall of temperature in passage from (α) to (c). On the first of these, the isotherm contains an independently existing region of layer formation $l_{AB}Kl_{BA}$ starting from the line of the binary system AB, with a critical point K

which is opposite the region of layer formation $l_1 K_1 l_2$, with critical point K_1 adjoining the triangle $l_1 l l_2$ of the three liquid phases. With falling temperature both of these regions with their critical points merge together initially and mutual intersection takes place subsequently. This moment is also represented in diagram b in which the region of layer formation $l_{AB} m l_1 l_2 n l_{BA}$ has two nodal points m and n, which with rising temperature are displaced in the direction of the binary system AB. On reaching the latter, the nodes disappear because the
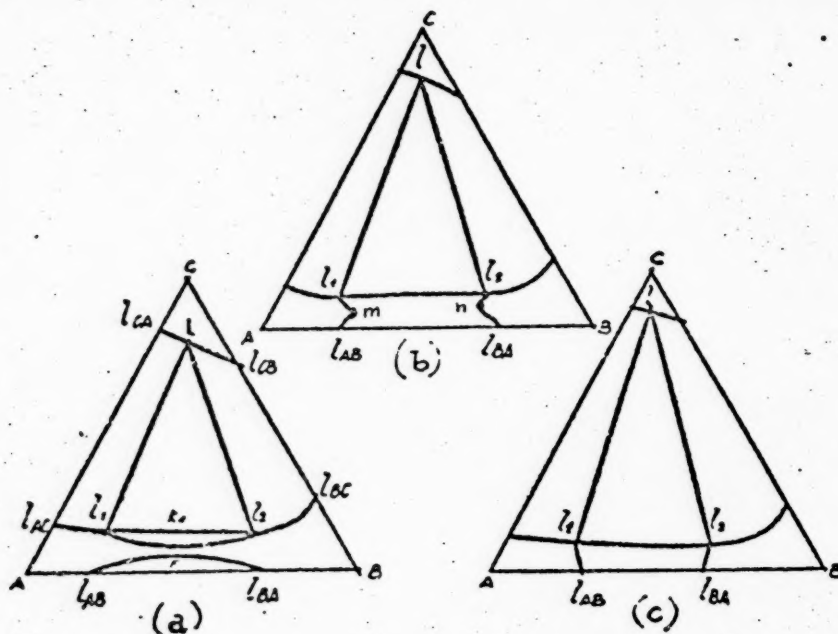
Fig. 4.

region of layer formation, contiguous to $l_1 l_2$ now with its stable portions $l_1 l_{AB}$ and $l_2 l_{BA}$ of the binodal curve will extend to the mutually saturated solutions l_{AB} and l_{BA} of the binary system AB. Such a position of the equilibrium fields is also illustrated in diagram c.

We shall now explain the significance of the sections running from the direction of the points of the binary system AB to the apex C. We plot a series of isotherms (Fig. 5), on the basis of a temperature – concentration prism, which correspond to the progressively decreasing temperatures t, t_1, t_2, t_3, t_4, and t_5. We select the sections x – c, y – c, z – c, and we plot their separate fields in Fig. 6, a, b, and c, the coordinates being temperature and concentration (C). The first of these gives, on the ordinates corresponding to the point x, the temperature of homogenization t_x, which will systematically decline in the section to the value of t_3, corresponding to the complex 1. Starting from the latter and right up to complex 2, the temperature of homogenization will
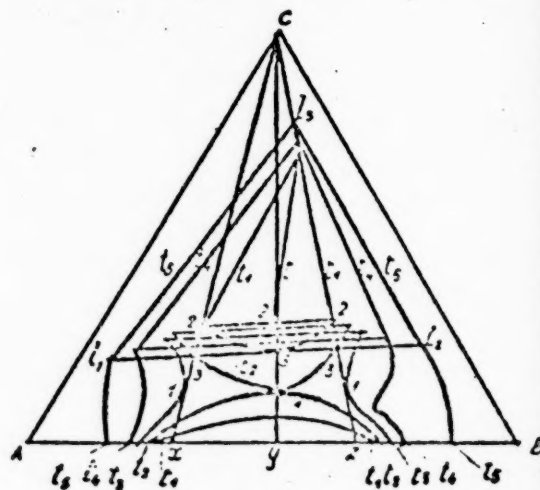
Fig. 5
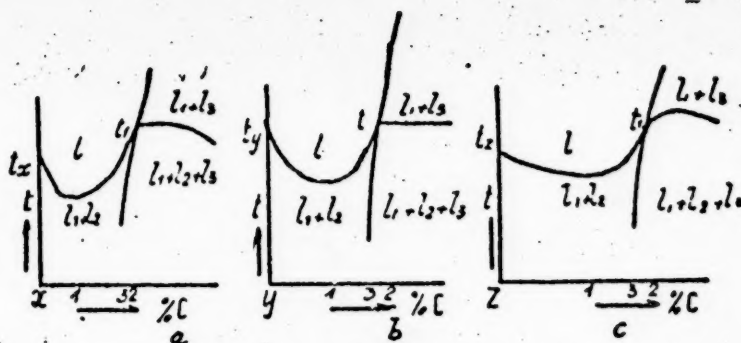
Fig. 6.

again rise, attaining a value t_1 corresponding to the maximum temperature of equilibrium of the three liquid phases in the given section. The homogenization line extends upwards from point 2; this line separates the homogenization field from 1 from the two-phase field $l_1 + l_3$; extending downwards from it on the right is a line separating the two-phase field from the field of three liquid phases, and finally, a line extending downwards to the left which separates the field of three liquid phases from the field of two liquid phases $l_1 + l_2$. In Fig. 5 the node $l_1 l_2$ is shown with a given selected slope, in which connection the distance between concentrations x and (2) will increase with displacement of the given sections from left to right, as is also indicated in Fig. 6, a and c, which relate to sections running from the concentration points y and z situated to the right of the composition point x. Although analogous, they differ from each other with regard to the temperatures of layer formation t_x, t_y, and t_z of the starting solutions x, y, and z, with regard to the higher temperatures t_1, t, t_1 of the three-phase liquid state, and with regard to the slope of the lines separating the field of the two-phase state $(l_1 + l_3)$ from the three-phase one. The latter is governed by the character of the intersection of the given sections with the surface of the three-phase state. Thus, we see from Fig. 5 that the section (x – c) cuts the left sides of the triangles of the three-phase state, in consequence of which from point t_1 (Fig. 6, a) the curve goes downwards at a slant and then proceeds extremely abruptly in conformity with the fact that the intersected surface has an extremely indefinite apex. In the section (y – c) we find at the start an almost horizontal portion of considerable length; the curve only slopes sharply on entering the branch surface. The section (z – c) exhibits a novel peculiarity. Intersecting the right sides of the triangles of the three phases, it meets initially the isotherms of progressively rising temperatures and only later, after attaining a certain isotherm of maximum temperature, will intersection occur with the isotherms of progressively falling temperatures. Hence, (Fig. 6, c), starting from point t_1 the curve moves upwards a little, reaches a maximum, and then begins to fall in the direction of lower temperatures.

Examination of the literature does not reveal any equilibrium diagrams similar to those described, and this may be accounted for on the one hand by the neglect of study of systems with three liquid phases in equilibrium, and on the other hand by the overlooking, to be frank, of the factors considered above. Schreinemakers, in considering the problem of the formation of a field of three liquid phases in the system succinonitrile – ether – water, suggests that the formation involves either the scheme of Fig. 7 or that of Fig. 8, and entirely ignores the possibility of existence of two independent regions of layer formation which extend toward each other from the direction of one of the binary enclosed systems and from the field of three liquid phases which initially intersect

each other, followed by displacement of the region of layer formation extending from the binary system by the region of layer formation developed in course of formation of the field of three, liquid phases. With the aim of experimentally verifying the correctness of our theory, we have studied three sections in the system succinonitrile – ether – water. The sections are drawn through the apex
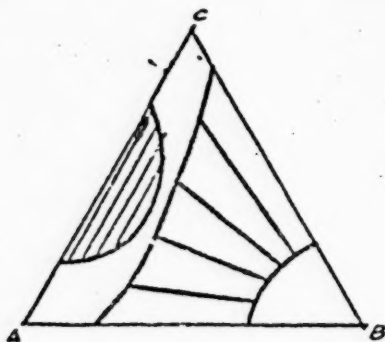
Fig. 7.
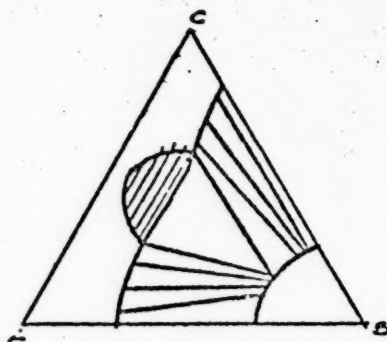
Fig. 8.

of the composition triangle corresponding to ether and the points of the binary system succinonitrile – water with 85, 62, and 50 wt. per cent water. Experimental determinations were made of the temperature of layer formation and of development of three liquid phases as a function of the ether content of the sections. These data are presented in the Table and plotted in Figs. 9, 10, and 11.
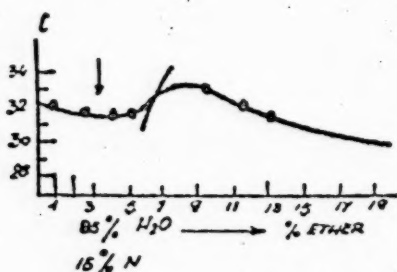
Fig. 9.
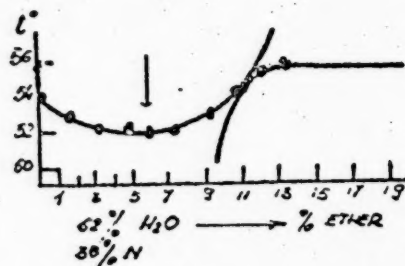
Fig. 10.

As can be seen from the tabulated material and from the diagrams, the addition of ether to the initial mixtures of succinonitrile and water at first lowers the homogenization temperature. This in itself is evidence of the presence of an independent region of layer formation penetrating into the composition triangle from the line of the binary system water – succinonitrile. The further conclusion may then be drawn that the formation of a field of three liquid phases does not correspond to the scheme of Fig. 7, and the diagram as a whole corresponds to the scheme set forth in Fig. 5. Notwithstanding the rather indefinite minimum present in all three sections, it can be established that with gradual decrease in the minimum, it approaches closer and
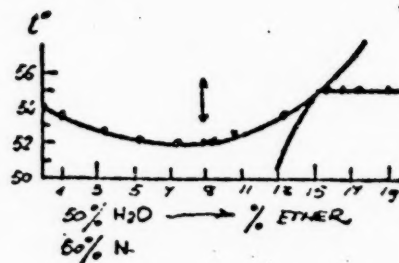
Fig. 11.

Temperature of Homogenization and Formation of Three Liquid Phases in Sections of the System Succinonitrile – Water – Ether

Expt. No.	Weight % ether	85% water 15% nitrile		65% water 35% nitrile		50% water 50% nitrile	
		Temperature					
		Layer formation	Formation of three liquid phases	Layer formation	Formation of three liquid phases	Layer formation	Formation of three liquid phases
1	0	32.2	–	53.8	–	54.0	–
2	1	31.9	–	53.0	–	53.5	–
3	2	31.6	–	52.5	–	53.1	–
4	3	31.4	–	52.1	–	52.8	–
5	4	31.5	–	51.9	–	52.5	–
6	5	31.5	–	51.8	–	52.3	–
7	6	32.0	–	51.8	–	52.2	–
8	6.5	32.4	–	–	–	52.1	–
9	7	32.9	32.9	51.9	–	52.0	–
10	8	–	33.3	52.2	–	52.0	–
11	9	–	33.2	52.6	–	52.0	–
12	10	–	32.8	53.3	–	52.2	–
13	11	–	32.4	54.1	–	52.5	–
14	12	–	31.9	–	54.9	52.9	–
15	13	–	31.5	–	55.3	53.3	–
16	14	–	31.2	–	55.3	53.9	–
17	15	–	30.9	–	–	54.8	–
18	16	–	30.6	–	55.2	–	55.0
19	17	–	30.3	–	–	–	55.0
20	18	–	30.1	–	55.1	–	55.0
21	19	–	–	–	–	–	55.0
22	20	–	–	–	–	–	55.0

closer to the initial point of the section with increasing per cent content of water. Thus, with a water content of 50 wt.% at the initial point, the minimum occurs at 8.5% ether and lies 2°C below the homogenization temperature of this point; but with an initial water content of 66 wt.% the minimum occurs at 3.5 wt.% ether and lies only 0.7° below the homogenization temperature. These relationships clearly indicate the displacement with falling temperature of the region of layer formation extending from the water – nitrile line by the region of layer formation extending from the equilibrium area of the three liquid phases.

SUMMARY

1. It is postulated that in multicomponent systems each binary layer formation has its own independent region of layer formation.

2. The possibility is indicated of displacement of one region of layer formation by another with change of temperature following their mutual intersection.

3. These concepts have been experimentally verified for the ternary system water – ether – succinonitrile, which is shown to contain an independent region of layer formation bound up with layer formation in the binary system water – succinonitrile and which is displaced with falling temperature by the

region of layer formation extending from the equilibrium area of the three liquid phases.

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THE POSITION OF THE MAXIMA
ON THE OPTICAL DENSITY/COMPOSITION CURVE
DURING CHANGE IN THE CONCENTRATION OF A
SYSTEM BY ADDITION OF A THIRD SUBSTANCE.

M. S. Barvinok

Change of Concentration of a System by Addition of Substances
Acting as Solvents During an Investigation of Cobalt Halides

It is known from the literature data [1] and our own observations that the absorption curves of individual complexes are influenced by the nature of the solvent. The change in the absorption of monochromatic light by the complex may be governed either by the molecules of solvent entering the solvated shell of the complex or by the displacement of halide ions from the complex by molecules of solvent. The possibility is not excluded that both factors operate at the same time. In an investigation of the system ($Co(ClO_4)_2$ + LiHal in one of the solvents, by the method of plotting of the composition/optical density diagram, we determine the composition of the complex without consideration of the solvated shell. Moreover, a change in the absorption of the complex may take place under the influence of a third substance if the molecules of the latter are able to displace the molecules of solvent from the solvated shell. In that case the absorption maximum will remain unchanged.

In the event of substitution of the halide in the complex by a molecule of a third substance, the maximum on the diagram will be shifted in the direction of a lower content of halide in the complex.

We have studied the position of the maxima on the optical density/composition curve of the system $Co(ClO_4)_2$ + LiCl in acetone using as third substance methyl alcohol, ethyl alcohol, and quinoline. Mixtures were prepared in the following manner:

Separate solutions were first prepared of 1) 0.005 mole of $Co(ClO_4)_2$ + LiCl in acetone, 2) 0.005 mole of LiCl in acetone, and 3) 0.005 mole methyl alcohol in acetone, 0.005 mole ethyl alcohol in acetone, and 0.005 mole quinoline in acetone.

The ratio of concentrations of the components in the system $Co(ClO_4)_2$ + LiCl + third substance are given in Table 2.

Isoconcentrates of methyl alcohol, ethyl alcohol, and quinoline were prepared. The concentrations of solutions of the system $Co(ClO_4)_2$ + LiCl in acetone are given in Table 1.

The total volume of the mixture of each solution of the isoconcentrates was 10 ml. For the first isoconcentrates, 2.5 ml of a solution of the third substance in acetone was used with 7.5 ml of the solution of $Co(ClO_4)_2$ + LiCl in acetone; for the second isoconcentrates, 5 ml of 0.005 molar solution of the third component in acetone was used with 5 ml of the solution of $Co(ClO_4)_2$ + LiCl in acetone; for the third isoconcentrates, 7.5 ml of 0.005 molar solution
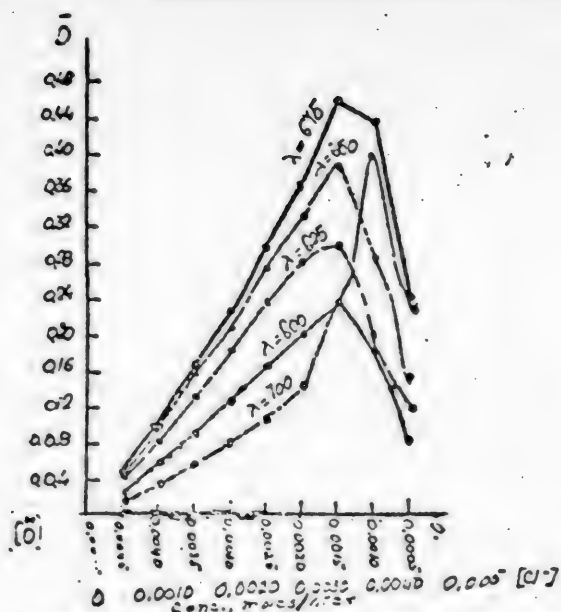
Fig. 1. Cobalt perchlorate-lithium chloride in acetone.
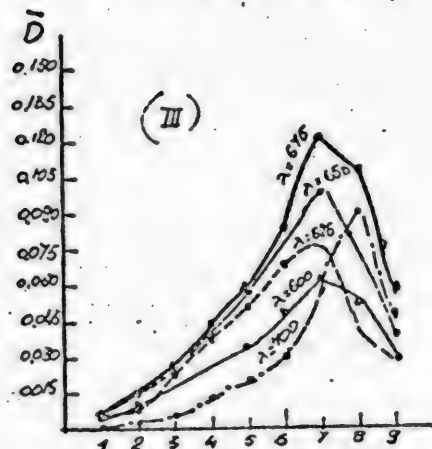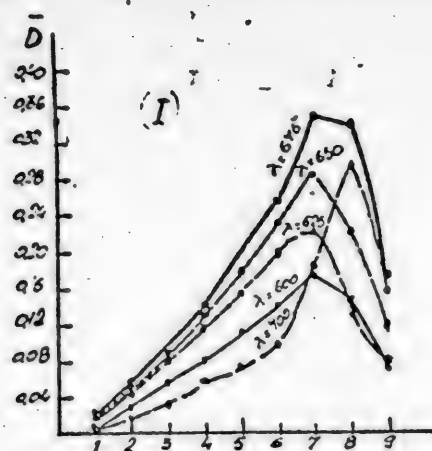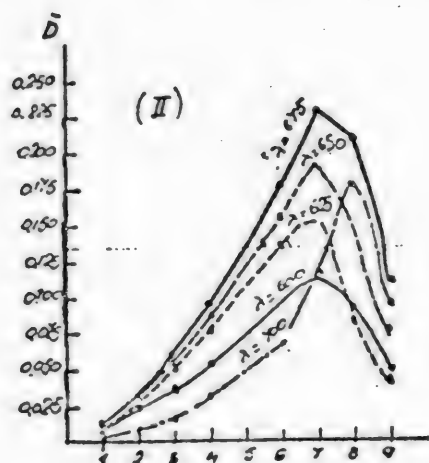
Fig. 2. $Co(ClO_4)_2$ + LiCl + CH_3OH in acetone (concentration of 0.005 mole per liter).

I - First isoconcentrate $[CH_3OH]$ = = $1.125 \cdot 10^{-3}$ moles/liter;

II - Second isoconcentrate $[CH_3OH]$ = = $2.5 \cdot 10^{-3}$ moles/liter;

III - Third isoconcentrate $[CH_3OH]$ = $3.75 \cdot 10^{-3}$ moles/liter.

Table 1. Optical Densities of Acetone Solutions of Cobalt Perchlorate in Presence of Lithium Chloride at 0.005 Molar Concentration

| Expt. No. | Composition of solutions | | | | Optical density D observed at wavelength λ (in mμ) | | | | | D at λ (in mμ) | | | | |
| | $Co(ClO_4)_2$ (in ml) | LiCl (ml) | Concentrations (in moles/l.) | | 600 | 625 | 650 | 675 | 700 | 600 | 625 | 650 | 675 | 700 |
			$Co(ClO_4)_2$	LiCl										
1	4.5	0.5	0.0045	0.0005	0.025	0.036	0.042	0.042	0.012	0.025	0.036	0.042	0.012	0.012
2	4.0	1.0	0.0040	0.0010	0.055	0.081	0.095	0.098	0.030	0.055	0.081	0.095	0.098	0.030
3	3.5	1.5	0.0035	0.0015	0.087	0.130	0.150	0.160	0.051	0.087	0.130	0.150	0.160	0.051
4	3.0	2.0	0.0030	0.0020	0.125	0.180	0.205	0.220	0.078	0.125	0.180	0.205	0.220	0.078
5	2.5	2.5	0.0025	0.0025	0.165	0.235	0.273	0.295	0.108	0.165	0.235	0.273	0.295	0.108
6	2.0	3.0	0.0020	0.0030	0.198	0.280	0.330	0.365	0.140	0.198	0.280	0.330	0.365	0.140
7	1.5	3.5	0.0015	0.0035	0.235	0.300	0.387	0.458	0.232	0.235	0.300	0.387	0.458	0.232
8	1.0	4.0	0.0010	0.0040	0.186	0.190	0.288	0.438	0.400	0.186	0.190	0.288	0.438	0.400
9	0.5	4.5	0.0005	0.0045	0.084	0.120	0.152	0.238	0.232	0.084	0.120	0.152	0.238	0.232

TABLE 2

Isoconcentrates of Methyl Alcohol.

$Co(ClO_4)_2$ + LiCl + CH_3OH; Total Concentration 0.005 moles/liter in Acetone

Expt. No.	Composition of solutions		D at λ (in mμ)				
	$Co(ClO_4)_2$ (moles/liter)	LiCl (moles/liter)	600	625	650	675	700

First isoconcentrate of methyl alcohol
$[CH_3OH] = 1.25 \cdot 10^{-3}$ mole/liter

1	$3.375 \cdot 10^{-3}$	$3.375 \cdot 10^{-4}$	0.008	0.017	0.018	0.018	0.005
2	3.10^{-3}	$7.5 \cdot 10^{-4}$	0.033	0.047	0.051	0.054	0.017
3	$2.625 \cdot 10^{-3}$	$1.125 \cdot 10^{-3}$	0.056	0.080	0.087	0.095	0.030
4	$2.25 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	0.081	0.117	0.131	0.140	0.049
5	$1.875 \cdot 10^{-3}$	$1.875 \cdot 10^{-3}$	0.110	0.157	0.179	0.195	0.072
6	$1.5 \cdot 10^{-3}$	$2.25 \cdot 10^{-3}$	0.140	0.200	0.233	0.260	0.101
7	$1.125 \cdot 10^{-3}$	$2.625 \cdot 10^{-3}$	0.175	0.225	0.285	0.350	0.188
8	$7.5 \cdot 10^{-4}$	3.10^{-3}	0.150	0.133	0.225	0.340	0.295
9	$3.375 \cdot 10^{-4}$	$3.375 \cdot 10^{-3}$	0.073	0.079	0.118	0.177	0.156

Second isoconcentrate of methyl alcohol
$[CH_3OH] = 2.5 \cdot 10^{-3}$ mole/liter

1	$2.25 \cdot 10^{-3}$	$2.5 \cdot 10^{-4}$	0.007	0.010	0.011	0.010	0.002
2	2.10^{-3}	5.10^{-4}	0.021	0.028	0.031	0.031	0.008
3	$1.75 \cdot 10^{-3}$	$7.5 \cdot 10^{-3}$	0.033	0.049	0.055	0.057	0.016
4	$1.5 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	0.052	0.076	0.085	0.093	0.031
5	$1.25 \cdot 10^{-3}$	$1.25 \cdot 10^{-3}$	0.072	0.105	0.118	0.129	0.047
6	1.10^{-3}	$1.5 \cdot 10^{-3}$	0.093	0.135	0.154	0.174	0.065
7	$7.5 \cdot 10^{-3}$	$1.75 \cdot 10^{-3}$	0.115	0.152	0.190	0.230	0.118
8	5.10^{-4}	2.10^{-3}	0.093	0.082	0.142	0.210	0.183
9	$2.5 \cdot 10^{-4}$	$2.25 \cdot 10^{-3}$	0.048	0.042	0.075	0.110	0.095

Third isoconcentrate of methyl alcohol
$[CH_3OH] = 3.75 \cdot 10^{-3}$ mole/liter

1	$1.125 \cdot 10^{-3}$	$1.25 \cdot 10^{-4}$	0.003	0.005	0.005	0.004	0
2	1.10^{-3}	$2.5 \cdot 10^{-4}$	0.009	0.008	0.014	0.015	0.002
3	$8.75 \cdot 10^{-4}$	$3.75 \cdot 10^{-4}$	0.016	0.023	0.025	0.026	0.005
4	$7.5 \cdot 10^{-4}$	5.10^{-4}	0.025	0.037	0.040	0.042	0.013
5	$6.25 \cdot 10^{-4}$	$6.25 \cdot 10^{-4}$	0.033	0.050	0.055	0.057	0.019
6	5.10^{-4}	$7.5 \cdot 10^{-4}$	0.047	0.068	0.078	0.083	0.030
7	$3.75 \cdot 10^{-4}$	$8.75 \cdot 10^{-4}$	0.061	0.075	0.097	0.120	0.065
8	$2.5 \cdot 10^{-4}$	1.10^{-3}	0.052	0.040	0.070	0.107	0.090
9	$1.25 \cdot 10^{-4}$	$1.125 \cdot 10^{-3}$	0.028	0.023	0.038	0.057	0.047

of the third substance in acetone were used with 2.5 ml of the solution of $Co(ClO_4)_2$ + LiCl in acetone. Thus, the total volume of each of these mixtures was 10 ml. The total molarity of such solutions was 0.005 mole.

Isoconcentrates of Methyl Alcohol.

As reported in the literature [2] the position of the maxima on the optical density/composition curves may alter with change in the total concentration of the solutions. Two maxima are shown in Fig. 1 at a total concentration of 0.05 molar of the solutions of the system $Co(ClO_4)_2$ + LiCl in acetone. One

TABLE 3

Isoconcentrates of Ethyl Alcohol

$Co(ClO_4)_2$ + LiCl + C_2H_5OH; total concentration of 0.005 mole/liter in acetone

Expt. No.	Composition of solutions		D at λ (in mμ)				
	$Co(ClO_4)_2$ (moles/liter)	LiCl (moles/liter)	600	625	650	675	700
First ethyl alcohol isoconcentrate: $[C_2H_5OH]$ = $1.25 \cdot 10^{-3}$ mole/liter							
1	$3.375 \cdot 10^{-3}$	$3.75 \cdot 10^{-4}$	0.015	0.026	0.028	0.030	0.010
2	2.10^{-3}	$7.5 \cdot 10^{-4}$	0.042	0.058	0.065	0.071	0.024
3	$2.625 \cdot 10^{-3}$	$1.125 \cdot 10^{-3}$	0.065	0.093	0.103	0.115	0.038
4	$2.25 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	0.090	0.131	0.147	0.166	0.059
5	$1.875 \cdot 10^{-3}$	$1.875 \cdot 10^{-3}$	0.123	0.181	0.205	0.232	0.086
6	$1.5 \cdot 10^{-3}$	$2.25 \cdot 10^{-3}$	0.150	0.223	0.256	0.295	0.113
7	$1.125 \cdot 10^{-3}$	$2.625 \cdot 10^{-3}$	0.183	0.233	0.298	0.375	0.213
8	$7.5 \cdot 10^{-4}$	3.10^{-3}	0.144	0.131	0.217	0.336	0.311
9	$3.75 \cdot 10^{-4}$	$3.375 \cdot 10^{-3}$	0.068	0.082	0.116	0.180	0.173
Second ethyl alcohol isoconcentrate: $[C_2H_5OH]$ = $2.5 \cdot 10^{-3}$ mole/liter							
1	$2.25 \cdot 10^{-3}$	$2.5 \cdot 10^{-4}$	0.011	0.014	0.015	0.016	0.005
2	2.10^{-3}	5.10^{-4}	0.026	0.036	0.039	0.043	0.015
3	$1.75 \cdot 10^{-3}$	$7.5 \cdot 10^{-3}$	0.041	0.058	0.065	0.073	0.025
4	$1.5 \cdot 10^{-3}$	1.10^{-3}	0.059	0.088	0.098	0.110	0.038
5	$1.25 \cdot 10^{-3}$	$1.25 \cdot 10^{-3}$	0.078	0.117	0.131	0.150	0.054
6	1.10^{-3}	$1.5 \cdot 10^{-3}$	0.102	0.150	0.170	0.196	0.074
7	$7.5 \cdot 10^{-3}$	$1.75 \cdot 10^{-3}$	0.121	0.159	0.200	0.249	0.138
8	5.10^{-4}	2.10^{-3}	0.096	0.081	0.140	0.215	0.202
9	$2.5 \cdot 10^{-4}$	$2.25 \cdot 10^{-3}$	0.047	0.043	0.073	0.112	0.106
Third ethyl alcohol isoconcentrate: $[C_2H_5OH]$ = $3.75 \cdot 10^{-3}$ mole/liter							
1	$1.125 \cdot 10^{-3}$	$1.25 \cdot 10^{-4}$	0.006	0.007	0.007	0.008	0.003
2	1.10^{-3}	$2.5 \cdot 10^{-4}$	0.013	0.020	0.021	0.023	0.008
3	$8.75 \cdot 10^{-4}$	$3.75 \cdot 10^{-4}$	0.022	0.033	0.035	0.039	0.013
4	$7.5 \cdot 10^{-4}$	5.10^{-4}	0.028	0.042	0.047	0.052	0.018
5	$6.25 \cdot 10^{-4}$	$6.25 \cdot 10^{-4}$	0.040	0.060	0.067	0.075	0.026
6	5.10^{-3}	$7.5 \cdot 10^{-4}$	0.048	0.075	0 083	0.094	0.033
7	$3.75 \cdot 10^{-4}$	$8.75 \cdot 10^{-4}$	0.060	0.075	0.098	0.125	0.073
8	$2.5 \cdot 10^{-4}$	1.10^{-3}	0.052	0.040	0.073	0.111	0.101
9	$1.25 \cdot 10^{-4}$	$1.125 \cdot 10^{-3}$	0.026	0.022	0.037	0.056	0.052

of these is on the optical density/composition curve at a wave length of 700 mμ. The composition of the complex corresponding to this maximum is given by the ratio m/n = 1:4. The other maximum is observed at shorter wave lengths – 600, 625, 650, 675 mμ. It arises from the presence in the system, apart from $CoCl_4^{--}$, of complexes with a lower content of chlorine ions.

In Fig. 2 are plotted three isoconcentrates of methyl alcohol for the system $Co(ClO_4)_2$ + LiCl + CH_3OH in acetone with a total concentration of 0.005 mole. The composition of the solutions and their optical densities are given in Table 2.

We see from Fig. 2 that the position of the maxima in all of the three isoconcentrates remains unchanged. Only a reduction in the optical density is observed. In the third isoconcentrate the solutions have a lower optical density than in the second, and in the second a lower density than in the first, due to the decrease in the concentration of the cobalt chloride complexes.
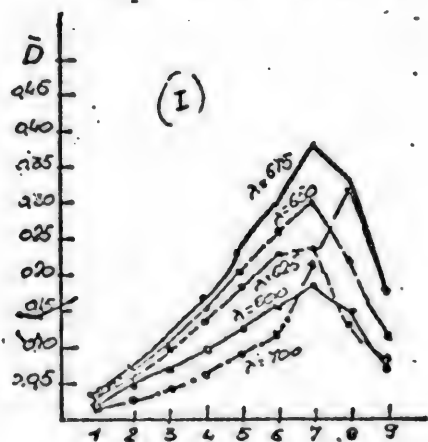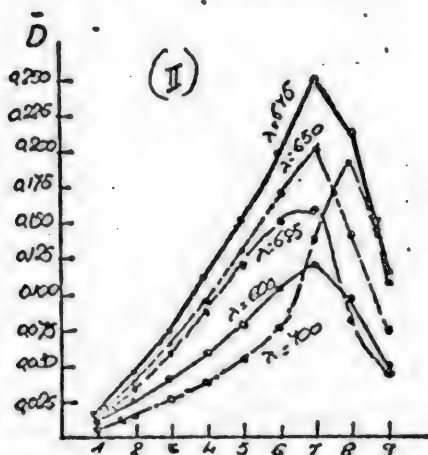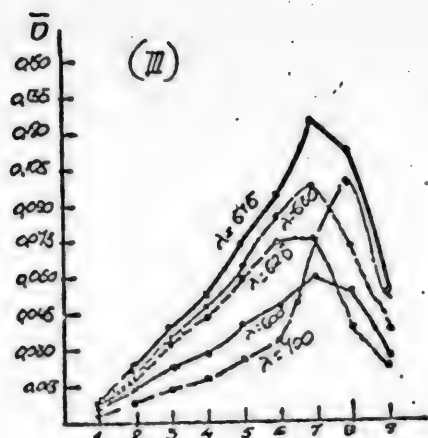
Fig. 3. $Co(ClO_4)_2$ + LiCl + C_2H_5OH in
acetone (concentration of 0.005 mole
per liter).

I-First isoconcentrate $[C_2H_5OH]$ = $1.125 \cdot 10^{-3}$ mole/l.;
II-Second isoconcentrate $[C_2H_5OH]$ = $2.5 \cdot 10^{-3}$ mole/l.;
III-third isoconcentrate $[C_2H_5OH]$ = $3.75 \cdot 10^{-3}$ mole/l.
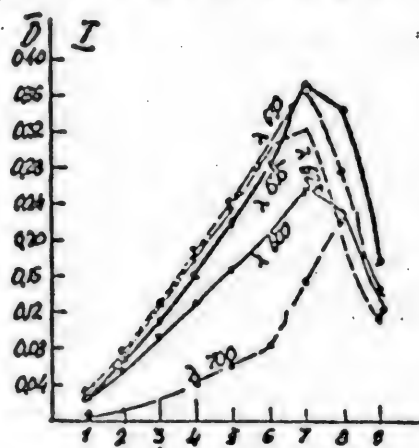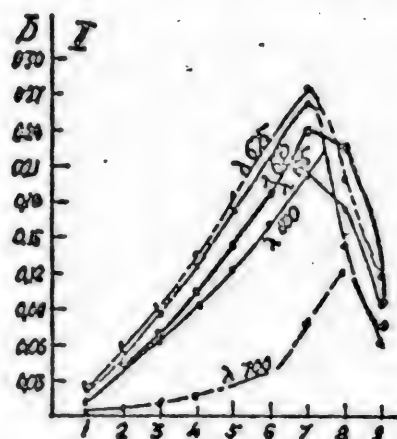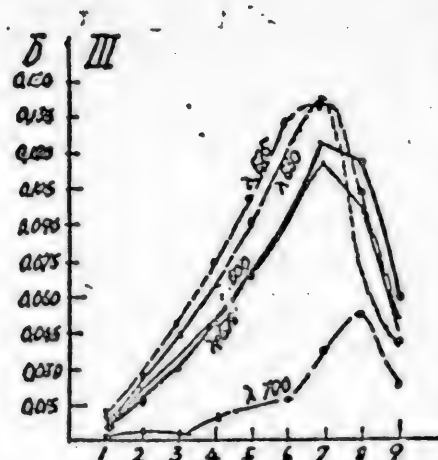
Fig. 4. $Co(ClO_4)_2$ + LiCl + quinoline
in acetone (concentration of 0.005
mole per liter)

I-First isoconcentrate $[quinoline]$ = $1.125 \cdot 10^{3}$
mole/l.; II-Second isoconcentrate $[quinoline]$ =
$2.5 \cdot 10^{-3}$ mole/l.; III-third isoconcentrate
$[quinoline]$ - $3.75 \cdot 10^{-3}$ mole/l.

TABLE 4

Quinoline Isoconcentrates

$Co(ClO_4)_2$ + LiCl + C_9H_7N, concentration 0.005 moles/liter in acetone

Expt. No.	Composition of solutions		D at λ (in mμ)				
	$Co(ClO_4)_2$ (moles/liter)	LiCl (moles/liter)	600	625	650	675	700
First quinoline isoconcentrate [C_9H_7N] = $1.25 \cdot 10^{-3}$ moles/liter							
1	$3.375 \cdot 10^{-3}$	$3.75 \cdot 10^{-4}$	0.025	0.033	0.032	0.025	0.005
2	3.10^{-3}	$7.5 \cdot 10^{-4}$	0.058	0.080	0.080	0.065	0.014
3	$2.625 \cdot 10^{-3}$	$1.125 \cdot 10^{-3}$	0.093	0.131	0.130	0.108	0.024
4	$2.25 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	0.150	0.185	0.187	0.162	0.044
5	$1.875 \cdot 10^{-3}$	$1.875 \cdot 10^{-3}$	0.168	0.242	0.245	0.217	0.062
6	$1.5 \cdot 10^{-3}$	$2.25 \cdot 10^{-3}$	0.211	0.305	0.315	0.282	0.084
7	$1.125 \cdot 10^{-3}$	$2.625 \cdot 10^{-3}$	0.260	0.325	0.368	0.374	0.157
8	$7.5 \cdot 10^{-4}$	3.10^{-3}	0.235	0.202	0.282	0.348	0.224
9	$3.75 \cdot 10^{-4}$	$3.375 \cdot 10^{-3}$	0.116	0.111	0.149	0.184	0.123
Second quinoline isoconcentrate [C_9H_7N] = $2.5 \cdot 10^{-3}$ moles/liter							
1	$2.25 \cdot 10^{-3}$	$2.5 \cdot 10^{-4}$	0.018	0.024	0.023	0.017	0.003
2	2.10^{-3}	5.10^{-4}	0.040	0.056	0.053	0.041	0.007
3	$1.75 \cdot 10^{-3}$	$7.5 \cdot 10^{-3}$	0.065	0.094	0.090	0.069	0.011
4	$1.5 \cdot 10^{-3}$	1.10^{-3}	0.094	0.138	0.132	0.106	0.018
5	$1.25 \cdot 10^{-3}$	$1.25 \cdot 10^{-3}$	0.125	0.185	0.177	0.143	0.026
6	1.10^{-3}	$1.5 \cdot 10^{-3}$	0.163	0.238	0.231	0.188	0.036
7	$7.5 \cdot 10^{-3}$	$1.75 \cdot 10^{-3}$	0.206	0.263	0.275	0.242	0.080
8	5.10^{-4}	2.10^{-3}	0.178	0.145	0.200	0.228	0.122
9	$2.5 \cdot 10^{-4}$	$2.25 \cdot 10^{-3}$	0.092	0.078	0.105	0.120	0.063
Third quinoline isoconcentrate [C_9H_7N] = $3.75 \cdot 10^{-3}$ moles/liter							
1	$1.125 \cdot 10^{-3}$	$1.25 \cdot 10^{-4}$	0.006	0.010	0.008	0.006	0
2	1.10^{-3}	$2.5 \cdot 10^{-4}$	0.022	0.029	0.026	0.019	0.003
3	$8.75 \cdot 10^{-4}$	$3.75 \cdot 10^{-3}$	0.033	0.048	0.043	0.030	0.003
4	$7.5 \cdot 10^{-4}$	5.10^{-3}	0.052	0.075	0.068	0.050	0.010
5	$6.25 \cdot 10^{-4}$	$6.25 \cdot 10^{-3}$	0.068	0.099	0.092	0.063	0.014
6	5.10^{-4}	$7.5 \cdot 10^{-3}$	0.092	0.132	0.122	0.090	0.018
7	$3.75 \cdot 10^{-4}$	$8.75 \cdot 10^{-3}$	0.115	0.140	0.143	0.123	0.037
8	$2.5 \cdot 10^{-4}$	1.10^{-3}	0.097	0.077	0.104	0.115	0.052
9	$1.25 \cdot 10^{-4}$	$1.125 \cdot 10^{-3}$	0.048	0.040	0.054	0.060	0.023

Isoconcentrates of Ethyl Alcohol

The solutions used for a study of ethyl alcohol isoconcentrates were prepared in a similar manner with the same total concentration of the solutions. Optical density/composition plots are shown in Fig. 3, and the composition of the solutions and their optical densities are presented in Table 3. It is seen from Fig. 3 that the position of the maxima in this case likewise remains unchanged. As in the case of the methyl alcohol isoconcentrates there is observed a fall in the optical density of solutions in passage from the first to the third solution, due to the fall in concentration of the cobalt chloride complex.

Quinoline Isoconcentrates

Solutions of quinoline isoconcentrates were prepared in the foregoing manner. Compositions are detailed in Table 4. The quinoline was redistilled before preparation of the solutions.

As shown in Fig. 4, the position of the maxima on the composition/optical density diagram does not change. The value of the optical density declines in passage from the first to the third isoconcentrate. The character of the spectral absorption, however, undergoes a change in the quinoline isoconcentrates. As known from the literature [1] and our own observations, the character of the absorption of complexes in solution depends upon the solvent. Cobalt chloride complexes in acetone have an absorption maximum at $\lambda = 675$ mμ. The solvent influences the character of the absorption of the complex because, in addition to ions of cobalt and chlorine (the ratio of which can be determined from the composition/optical density diagram), molecules of solvent also enter into the composition of the complex.

In the quinoline isoconcentrates the maximum absorption of the complexes is shifted in the direction of shorter wave lengths. This displacement, as we see from Fig. 4, is intensified with increasing concentration of quinoline. In the first isoconcentrate with the lowest concentration of quinoline, the maximum absorption is shifted into the region of 650-625 mμ, and finally in the third isoconcentrate with the highest content of quinoline the absorption maximum moves into the region of 625-659 mμ. Since at the same time there is no change in the position of the maxima of absorption on the composition/optical density curves, the change in the character of the absorption is not accompanied in this case by displacement of chlorine ions from the cobalt chloride complexes by molecules of quinoline. Molecules of quinoline evidently penetrate into the coordination sphere of the complex, forming a compound of the type of $[CoQu_2Cl_4]^{--}$ where Qu denotes quinoline. We had previously investigated the binary system $CoCl_2$ + quinoline in acetone at a total concentration of 0.005 mole. On the optical density/composition curves a maximum is obtained corresponding to m/n = 1:1, i.e., one molecule of quinoline is required for each molecule of $CoCl_2$. If we take into consideration the fact that $CoCl_4^{--}$ complexes are formed in acetone solutions of cobalt chloride, then the complex $[CoQu_2Cl_4]^{--}$ must be present in the solution, and this also brings about a change in the character of the absorption in quinoline isoconcentrates.

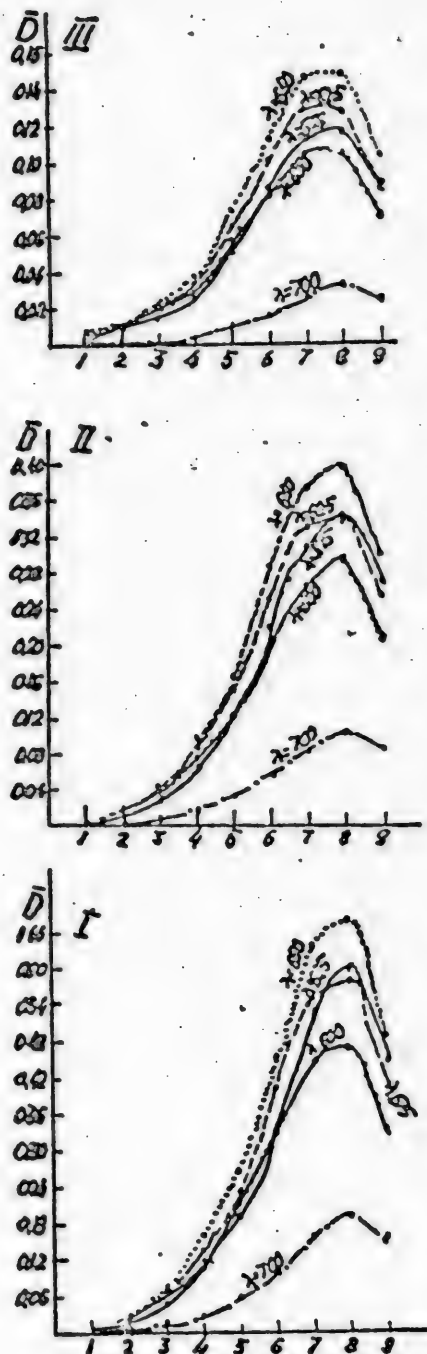Fig. 5. $Co(ClO_4)_2$ + LiCl + + acetone   in ethyl alcohol (total concentration 0.05 mole/liter).
I - $[CH_3 \cdot CO \cdot CH_3]$ = $1.25 \cdot 10^{-2}$ mole/l.
II - $[CH_3 \cdot COCH_3]$ = $2.5 \cdot 10^{-2}$ mole/l.
III - $[CH_3COCH_3]$ = $3.75 \cdot 10^{-2}$ mole/l.

TABLE 5

Acetone Isoconcentrates

$Co(ClO_4)_2$ + LiCl + Acetone in Ethyl Alcohol; Total Concentration 0.05 moles/l.

Expt. No.	Composition of solution $Co(ClO_4)_2$	LiCl	D at λ (in mμ) 600	625	650	675	700
First acetone isoconcentrate $[CH_3 \cdot CO \cdot CH_3]$ = $1.25 \cdot 10^{-2}$ moles/liter								
1	$3.375 \cdot 10^{-2}$	$3.75 \cdot 10^{-3}$	0.010	0.008	0.009	0.006	0.002
2	3.10^{-2}	$7.5 \cdot 10^{-3}$	0.025	0.026	0.028	0.019	0.003
3	$2.625 \cdot 10^{-2}$	$1.125 \cdot 10^{-2}$	0.060	0.063	0.066	0.047	0.010
4	$2.25 \cdot 10^{-2}$	$1.5 \cdot 10^{-2}$	0.114	0.133	0.148	0.115	0.027
5	$1.875 \cdot 10^{-2}$	$1.875 \cdot 10^{2}$	0.202	0.237	0.264	0.198	0.052
6	$1.5 \cdot 10^{-2}$	$2.25 \cdot 10^{-2}$	0.333	0.399	0.454	0.357	0.098
7	$1.125 \cdot 10^{-2}$	$2.625 \cdot 10^{-2}$	0.447	0.549	0.633	0.532	0.158
8	$7.5 \cdot 10^{-3}$	3.10^{-2}	0.469	0.577	0.677	0.599	0.192
9	$3.75 \cdot 10^{-3}$	$3.375 \cdot 10^{-2}$	0.334	0.407	0.485	0.450	0.155
Second acetone isoconcentrate $[CH_3 \cdot CO \cdot CH_3]$ = $2.5 \cdot 10^{-2}$ moles/liter								
1	$2.25 \cdot 10^{-2}$	$2.5 \cdot 10^{-3}$	0.004	0.003	0.004	0.002	0
2	2.10^{-2}	5.10^{-3}	0.015	0.016	0.017	0.012	0.001
3	$1.75 \cdot 10^{-2}$	$7.5 \cdot 10^{-2}$	0.036	0.039	0.040	0.029	0.006
4	$1.5 \cdot 10^{-2}$	1.10^{-2}	0.073	0.085	0.093	0.066	0.016
5	$1.25 \cdot 10^{-2}$	$1.25 \cdot 10^{-2}$	0.122	0.146	0.164	0.120	0.029
6	1.10^{-2}	$1.5 \cdot 10^{-2}$	0.204	0.247	0.283	0.215	0.054
7	$7.5 \cdot 10^{-2}$	$1.75 \cdot 10^{-2}$	0.263	0.324	0.372	0.304	0.080
8	5.10^{-3}	2.10^{-2}	0.293	0.339	0.397	0.341	0.101
9	$2.5 \cdot 10^{-3}$	$2.25 \cdot 10^{-2}$	0.204	0.252	0.296	0.266	0.084
Third acetone isoconcentrate $[CH_3 \cdot CO \cdot CH_3]$ = $3.75 \cdot 10^{-2}$ moles/liter								
1	$1.125 \cdot 10^{-2}$	$1.25 \cdot 10^{-3}$	0.007	0.005	0.005	0.003	0.001
2	1.10^{-2}	$2.5 \cdot 10^{-3}$	0.011	0.010	0.011	0.008	0.002
3	$8.75 \cdot 10^{-3}$	$3.75 \cdot 10^{-3}$	0.020	0.020	0.022	0.014	0.002
4	$7.5 \cdot 10^{-3}$	5.10^{-3}	0.029	0.033	0.035	0.025	0.005
5	$6.25 \cdot 10^{-3}$	$6.25 \cdot 10^{-3}$	0.056	0.065	0.072	0.052	0.010
6	5.10^{-3}	$7.5 \cdot 10^{-3}$	0.082	0.100	0.112	0.083	0.015
7	$3.75 \cdot 10^{-3}$	$8.75 \cdot 10^{-3}$	0.105	0.128	0.145	0.111	0.026
8	$2.5 \cdot 10^{-3}$	1.10^{-2}	0.105	0.129	0.148	0.118	0.032
9	$1.25 \cdot 10^{-3}$	$1.125 \cdot 10^{-2}$	0.070	0.088	0.103	0.085	0.023

Acetone Isoconcentrates of the System $Co(ClO_4)_2$ + LiCl in Ethyl Alcohol

Observations on the ethyl alcohol isoconcentrates of the system $Co(ClO_4)_2$ + LiCl in acetone show that addition of ethyl alcohol does not bring about a change in the character of the absorption such as occurred in the case of the quinoline isoconcentrates. However, we know that the character of absorption of solutions of cobalt chloride in ethyl alcohol differs from that of solutions of cobalt chloride in acetone. The latter have an absorption maximum at λ = 675, while solutions in ethyl alcohol have a maximum at λ = 650 mμ. It might be assumed that at the given concentrations the ethyl alcohol molecules cannot displace the acetone molecules from the solvated shell of the complex. It was of interest to examine the ability of acetone molecules to displace ethyl alcohol molecules from the solvated shell of the complex. For this purpose, three isoconcentrates of the system $Co(ClO_4)_2$ + LiCl + acetone in ethyl alcohol were prepared by the above method. (The ethyl alcohol was used in the absolutely anhydrous form.) Results of measurements of the optical densities of the solutions are listed in Table 5 and plotted in Fig. 5.

We see from Fig. 5 that no change occurs in the position of the maxima on the optical density /composition curves. In all three cases the maximum absorption is at $\lambda = 650$ mμ, which is characteristic of solutions of cobalt chloride in ethyl alcohol. Notwithstanding that the concentration of acetone molecules in the solutions of the acetone isoconcentrates is 10 times greater than the concentration of ethyl alcohol molecules in the solutions of ethyl alcohol isoconcentrates, no change in the character of the absorption is observed. We may therefore conclude that at the given concentrations the molecules of acetone are incapable of displacing the molecules of ethyl alcohol from the solvated shell. The change in the character of the maxima of the absorption curves of the acetone isoconcentrates is noteworthy. In passing from the first to the third isoconcentrate the maxima become more obtuse while their position remains unchanged.

In the isoconcentrates of ethyl alcohol in acetone solutions, the position and acuteness of the maxima on the curves remain substantially unchanged. This is due to the dissociation of cobalt chloride complexes in ethyl alcohol solution being more sensitive to dilution than is the case with the acetone solution. For if we assume that the change in the character of the maxima is dependent upon the reaction of the cobalt chloride complexes with acetone molecules, this should be reflected in changes in the absorption spectra. In that event the absorption maximum should be shifted in the direction of longer wave lengths in passing from the first to the third isoconcentrates, and no observations to this effect have been made.

SUMMARY

1. A study was made of the position of the maxima on the composition/optical density curves of the system $Co(ClO_4)_2$ + LiCl in acetone and ethyl alcohol, varying the concentration of the system by addition of substances acting as solvents for cobalt halides.

2. The position of the maxima remains unchanged on addition of methyl alcohol, ethyl alcohol, and quinoline to the acetone solutions, and also on addition of acetone to the alcoholic solutions.

3. Addition of quinoline to the system $Co(ClO_4)_2$ + LiCl in acetone is accompanied by a change in the character of the absorption spectrum, indicating interaction between the cobalt halide complex $CoCl_4^{--}$ and quinoline molecules.

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SPECTROPHOTOMETRIC STUDY OF COBALT (II)

HALIDE COMPLEXES IN BUTYL ALCOHOL

M. S. Barvinok

Numerous studies have been made of the solutions of the halides (chlorides, bromides, and iodides) of divalent cobalt. Interest in these solutions was aroused, as we know, by the change in color with different solvents and with varying concentrations and temperatures. The influence of these factors on the color of the solutions is bound up with the change of color of the solid products of addition of molecules of solvent to cobalt halides as modified by the content of addenda. Thus, cobalt halides containing six addenda (for example, H_2O, CH_3OH, C_2H_5OH, etc.) are red, while those containing two addenda are blue [1].

These facts led to the assumption that in the red solutions the cobalt ion is present in the form of $[CoR_6]^{++}$ and in the blue solutions in the form of $[CoR_2]^{++}$. Moreover, studies of the properties of solutions of halides of divalent cobalt (anodic migration, absorption spectra, molecular weights) pointed to the presence in all these cases of complex ions of cobalt with halogen. The composition of these complexes was not established by direct methods. The most probable form is $CoCl_4^{--}$. Much interest is associated with the study of complexes in solution since they provide a greater insight into those complex transformations taking place in solutions under the influence of changes in solvent, concentration, and temperature, and since they have great practical importance in analytical chemistry.

Alcohol solutions of cobalt chloride and bromide have been studied by many investigators, but solutions of cobalt iodide have been comparatively little studied. As previously shown [2], the ability to form complexes in a homologous series of normal alcohols increases from methyl alcohol to amyl alcohol in the case of the halides of divalent cobalt. In amyl alcohol, for example, solutions with a blue color are formed at high dilutions of cobalt chloride; in methyl alcohol the blue color of cobalt chloride is only developed at room temperature in very concentrated solutions.

By a systematic study of the composition of halide complexes in alcohol solutions, it should therefore be possible to follow the influence of the complexity of the alcohol molecules upon the process of complex formation in solutions. Previous investigations [3] dealt with the composition of cobalt (II)-halide complexes in methyl, ethyl, and propyl alcohols. The present paper considers solutions of halides of divalent cobalt in butyl alcohol. The composition of the complexes in solution has been studied by the method of physico-chemical analysis, the property selected for examination being the optical density [4].

EXPERIMENTAL

The optical density was measured with the Beckmann spectrophotometer at temperatures of $+20°$ to $-1°$. It is known that the perchlorates have a greater complex-forming tendency; consequently the cobalt preparation chosen for this study was $Co(ClO_4)_2 \cdot 6H_2O$, prepared by the previously described method [3].

Chemically pure normal butyl alcohol was dehydrated with metallic calcium by the literature method [5]. Formation of cobalt (II)-halide complexes is accompanied by strong absorption in the 600-725 mμ region, and the absorption is shifted in the direction of higher wave lengths in passing from the chloride to the iodide complexes. Solutions in butyl alcohol were therefore studied at 600, 625, 650, 675, 700, and 725 mμ.

A. Cobalt (II)-Chloride Complexes

Mixtures of solutions of $Co(ClO_4)_2$ and LiCl with a constant volume of 5 ml were prepared in concentration of 0.05 molar for the purpose of studying the composition of cobalt (II)-chloride complexes. Lithium chloride was prepared in the manner previously described [3]. Mixtures of the compositions shown in Table 1 were prepared. The value of $\bar{D}$ was calculated as the difference between the

TABLE 1

Optical Densities of Solutions of Cobalt Perchlorate in Presence of Lithium Chloride in Butyl Alcohol

	Composition of solutions				Optical density at (in mu)				D at λ (in mμ)			
	in ml		moles/liter									
	$Co(ClO_4)_2$	LiCl	$Co(ClO_4)_2$	LiCl	600	625	650	675	600	625	650	675
1	4.5	0.5	0.045	0.005	0.028	0.025	0.023	0.016	0.004	0.006	0.007	0.003
	4.5	0	0.045	–	0.024	0.019	0.016	0.013	–	–	–	–
2	4.0	1.0	0.040	0.010	0.049	0.048	0.019	0.034	0.026	0.030	0.003	0.022
	4.0	0	0.040	–	0.023	0.018	0.016	0.012	–	–	–	–
3	3.5	1.5	0.035	0.015	0.098	0.098	0.101	0.080	0.073	0.083	0.086	0.069
	3.5	0	0.035	–	0.020	0.015	0.015	0.011	–	–	–	–
4	3.0	2.0	0.030	0.020	0.180	0.207	0.228	0.178	0.163	0.193	0.217	0.170
	3.0	0	0.030	–	0.017	0.014	0.011	0.008	–	–	–	–
5	2.5	2.5	0.025	0.025	0.325	0.395	0.440	0.363	0.311	0.385	0.430	0.356
	2.5	0	0.025	–	0.014	0.010	0.010	0.007	–	–	–	–
6	2.0	3.0	0.020	0.030	0.540	0.670	0.760	0.656	0.530	0.662	0.752	0.650
	2.0	0	0.020	–	0.010	0.008	0.008	0.006	0.002	–	–	–
7	1.5	3.5	0.015	0.035	0.770	0.960	0.130	1.040	0.760	0.955	1.124	1.036
	1.5	0	0.015	–	0.010	0.005	0.006	0.004	–	–	–	–
8	1.0	4.0	0.010	0.040	0.819	1.050	1.240	1.200	0.811	1.046	1.276	1.197
	1.0	0	0.010	–	0.008	0.004	0.004	0.003	–	–	–	–
9	0.5	4.5	0.005	0.045	1.610	0.760	0.920	0.940	0.606	0.758	0.918	0.938
	0.5	0	0.005	–	0.004	0.002	0.002	0.002	–	–	–	–

optical densities of solutions of $Co(ClO_4)_2$ + LiCl and of $Co(ClO_4)_2$ (the optical density of the LiCl solution in this region of the spectrum is zero) when using a constant concentration of cobalt perchlorate. The maximum or minimum on the optical density/composition curve is an indication of the composition of the complex corresponding to this maximum or minimum of absorption [4]. As shown in Fig. 1, which is an optical density/composition plot, the maximum corresponds to 0.010 mole of $Co(ClO_4)_2$ and 0.040 mole of LiCl, which corresponds to the complex containing $CoCl_4^{--}$. This maximum is particularly sharp at $\lambda = 675$ mμ.

B. Cobalt (II) – Bromide Complexes

The composition of cobalt (II) – bromide complexes in butyl alcohol was

TABLE 2

Optical Densities of Solutions of Cobalt Perchlorate in Presence of Lithium Bromide in Butyl Alcohol

| Expt. No. | Composition of solutions | | | | Optical density at λ (in mμ) | | | | | D at λ (in mμ) | | | | |
| | in ml | | in moles/l. | | | | | | | | | | | |
	$Co(ClO_4)_2$	LiBr	$Co(ClO_4)_2$	LiBr	600	625	650	675	700	600	625	650	675	700
1	4.5	0.5	0.045	0.005	0.025	0.018	0.018	0.015	0.008	0.001	0.001	0.002	0.002	0.001
	4.5	0	0.045	–	0.024	0.019	0.016	0.013	0.009	–	–	–	–	–
2	4.0	1.0	0.040	0.010	0.035	0.030	0.028	0.025	0.012	0.012	0.012	0.012	0.013	0.003
	4.0	0	0.040	–	0.023	0.018	0.016	0.012	0.009	–	–	–	–	–
3	3.5	1.5	0.035	0.015	0.046	0.047	0.046	0.048	0.018	0.026	0.032	0.031	0.037	0.010
	3.5	0	0.035	–	0.020	0.015	0.015	0.011	0.008	–	–	–	–	–
4	3.0	2.0	0.030	0.020	0.070	0.082	0.082	0.082	0.031	0.053	0.068	0.071	0.074	0.029
	3.0	0	0.030	–	0.017	0.014	0.011	0.008	0.002	–	–	–	–	–
5	2.5	2.5	0.025	0.025	0.110	0.140	0.144	0.150	0.060	0.096	0.130	0.134	0.143	0.058
	2.5	0	0.025	–	0.014	0.010	0.010	0.007	0.012	–	–	–	–	–
6	2.0	3.0	0.020	0.030	0.164	0.218	0.226	0.243	0.103	0.154	0.210	0.218	0.237	0.101
	2.0	0	0.020	–	0.010	0.008	0.008	0.006	0.002	–	–	–	–	–
7	1.5	3.5	0.015	0.035	0.202	0.278	0.295	0.323	0.154	0.192	0.273	0.289	0.319	0.152
	1.5	0	0.015	–	0.010	0.005	0.006	0.004	0.002	–	–	–	–	–
8	1.0	4.0	0.010	0.040	0.218	0.308	0.330	0.362	0.195	0.210	0.304	0.326	0.359	0.193
	1.0	0	0.010	–	0.008	0.004	0.004	0.003	0.002	–	–	–	–	–
9	0.5	4.5	0.005	0.045	0.148	0.220	0.242	0.275	0.162	0.144	0.218	0.240	0.273	0.162
	0.5	0	0.005	–	0.004	0.002	0.002	0.002	0	–	–	–	–	–

examined by measurements on a series of solutions prepared by the above method. The lithium bromide was prepared by the previously described method. Mixtures of solutions of $Co(ClO_4)_2$ + LiBr in butyl alcohol with a total concentration of 0.05 molar were prepared as detailed in Table 2. Figure 2 is the optical density/composition plot. The maximum of the optical density corresponds to the composition 0.010 mole of $Co(ClO_4)_2$ and 0.040 mole of LiBr, which corresponds to the $CoBr_4^{--}$ complex.

In this case the sharp maximum constituted by the intersection of the two branches of the curve is located at $\lambda = 700$ mμ.

C. Cobalt (II) – Iodide Complexes

The composition of the complexes was examined by the method of physico-chemical analysis, using a series of solutions of $Co(ClO_4)_2$ + LiI in butyl alcohol prepared by mixing solutions of cobalt perchlorate with solutions of lithium iodide in various proportions. The alcohol solutions of lithium iodide were prepared from a Kahlbaum preparation of lithium iodide, the composition of which was checked by analysis. The total volume of each of the solutions of the system $Co(ClO_4)_2$ + LiI was 5 ml, the total concentration for the first series was 0.3 mole, for the second series 0.15 mole. Developemnt of absorption in the 600-725 mμ region for the alcohol solutions of the cobalt-iodide system occured at higher concentrations than was

the case for the cobalt-chloride and cobalt-bromide complexes [2]. Solutions were accordingly prepared with a total concentration of 0.3 mole (first series). Data for the optical densities of solutions of various compositions (first series) are set out in Table 3. Optical density/composition curves are plotted in Fig. 3 for wave lengths of 650, 675, 700, and 725 mμ

A sharp maximum appears in Fig. 3 at λ = 650, 675, and 700 mμ, formed by the intersection of the two branches of the curve, and corresponds to the mixture of 0.030 mole $Co(ClO_4)_2$ and 0.120 mole LiI, which corresponds to the CoI_4^{--} complex.

At longer wave lengths (725 mμ), however, no maximum is observed and the optical density continues to increase. This points to the existence of a complex richer in iodine. It is characteristic of the absorption of complexes with higher contents of halogens that it is shifted
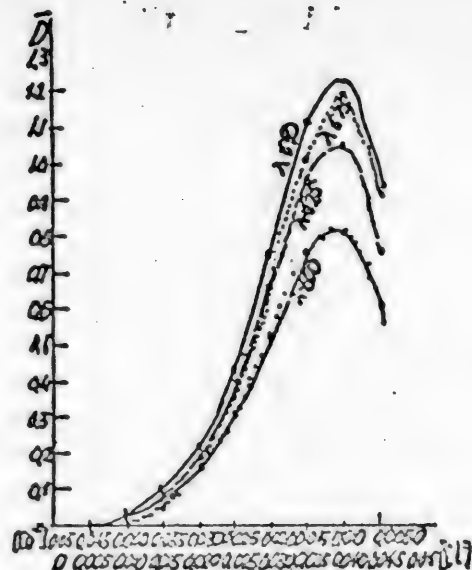

Fig. 1. Cobalt perchlorate + lithium chloride in butyl alcohol. Concentration 0.05 mole/1.

TABLE 3

Optical Densities of Solutions of Cobalt Perchlorate in Presence of Lithium Iodide in Butyl Alcohol

|	Composition of solutions				Optical density at (in mμ)				D at λ (in mμ)			
	in ml		moles/liter									
	$Co(ClO_4)_2$	LiI	$Co(ClO_4)_2$	LiI	650	675	700	725	650	675	700	725
1 {	4.5	0.5	0.27	0.03	0.100	0.073	0.048	0.030	0	0	0	0
	4.5	0	0.27	0	0.100	0.073	0.048	0.030	–	–	–	–
2 {	4.0	1.0	0.24	0.06	0.105	0.080	0.057	0.034	0.017	0.015	0.014	0.006
	4.0	0	0.24	0	0.088	0.065	0.043	0.028	–	–	–	–
3 {	3.5	1.5	0.21	0.09	0.124	0.100	0.078	0.046	0	0.045	0.043	0.021
	3.5	0	0.21	0	0.124	0.055	0.035	0.025	–	–	–	–
4 {	3.0	2.0	0.18	0.12	0.175	0.148	0.125	0.075	0.114	0.103	0.092	0.058
	3.0	0	0.18	0	0.061	0.045	0.033	0.017	–	–	–	–
5 {	2.5	2.5	0.15	0.15	0.270	0.242	0.222	0.132	0.218	0.206	0.194	0.123
	2.5	0	0.15	0	0.052	0.036	0.028	0.015	–	–	–	–
6 {	2.0	3.0	0.12	0.18	0.380	0.355	0.340	0.217	0.337	0.324	0.316	0.204
	2.0	0	0.12	0	0.043	0.031	0.024	0.013	–	–	–	–
7 {	1.5	3.5	0.09	0.21	0.522	0.550	0.495	0.340	0.490	0.526	0.480	0.331
	1.5	0	0.09	0	0.032	0.024	0.015	0.009	–	–	–	–
8 {	1.0	4.0	0.06	0.24	0.635	0.680	0.650	0.470	0.612	0.663	0.639	0.462
	1.0	0	0.06	0	0.023	0.017	0.011	0.008	–	–	–	–
9 {	0.5	4.5	0.03	0.27	0.580	0.650	0.638	0.480	0.568	0.642	0.632	0.476
	0.5	0	0.03	0	0.012	0.008	0.006	0 004	–	–	–	–
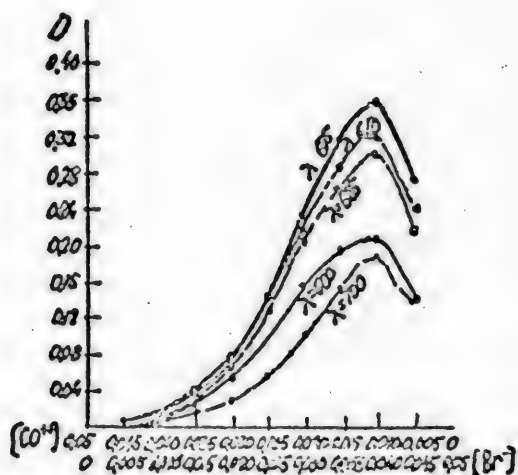
Fig. 2. Coblat perchlorate +
lithium bromide in butyl alcohol.
Concentration 0.05 mole/liter
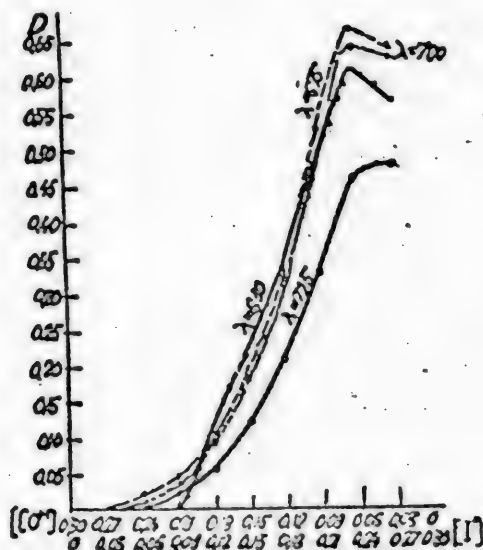

Fig. 3. Cobalt perchlorate + lith-
ium iodide in butyl alcohol. Con-
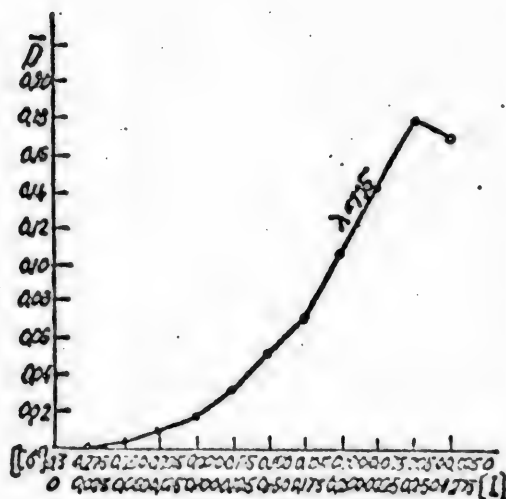centration 0.3 mole/liter.

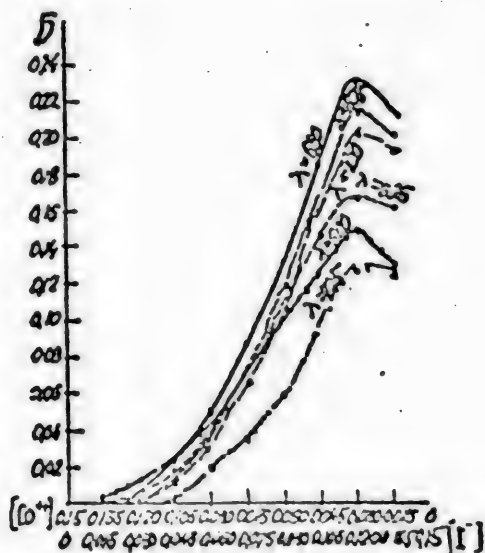Fig. 4. $Co(ClO_4)_2$ + LiI in butyl
alcohol. Concentration 0.3 mole/$\underline{1}$.

Fig. 5. $Co(ClO_4)_2$ + LiI in butyl
alcohol. Concentration 0.15 mole/$\underline{1}$.

TABLE 4

Optical Densities of Solutions of Cobalt Perchlorate in Presence of Lithium Iodide in Butyl Alcohol

Expt. No.	Composition of solutions				Optical density in mμ	D at λ, in mμ.
	in ml		in moles/liter		725	725
	$Co(ClO_4)_2$	LiI	$Co(ClO_4)_2$	LiI		
1	5.5	0.5	0.275	0.025	0.020	—
	5.5	0	0.275	—	0.020	0
2	5.0	1.0	0.250	0.050	0.020	—
	5.0	0	0.250	—	0.018	0.002
3	4.5	1.5	0.225	0.075	0.023	—
	4.5	0	0.225	—	0.023	0.010
4	4.0	2.0	0.200	0.100	0.032	—
	4.0	0	0.200	—	0.015	0.017
5	3.5	2.5	0.175	0.125	0.044	—
	3.5	0	0.175	—	0.012	0.032
6	3.0	3.0	0.150	0.150	0.061	—
	3.0	0	0.150	—	0.007	0.054
7	2.5	3.5	0.125	0.175	0.082	—
	2.5	0	0.125	—	0.010	0.072
8	2.0	4.0	0.100	0.200	0.115	—
	2.0	0	0.100	—	0.008	0.107
9	1.5	4.5	0.075	0.225	0.150	—
	1.5	0	0.075	—	0.006	0.144
10	1.0	5.0	0.050	0.250	0.188	—
	1.0	0	0.050	—	0.007	0.181
11	0.5	5.5	0.025	0.275	0.180	—
	0.5	0	0.025	—	0.007	0.173

towards the long-wave region of the spectrum. We also observed this phenomenon in the case of cobalt-chloride complexes [2]. The composition of the complex giving rise to the increase in optical density at $\lambda = 725$ mμ was studied with a series of solutions with a total concentration of 0.3 mole, and containing molar ratios of $Co(ClO_4)_2$ to LiI greater than 1:4. Measurements of the optical densities of these solutions revealed that the maximum on the optical density/composition curve occurs at a ratio corresponding to $m/n = 1/5$, i.e., five ions of iodine per ion of cobalt, which corresponds to the complex CoI_5^{---}, as shown in Table 4 and Fig. 4. It should be noted that two double salts of the type of Cs_5CoCl_5 are known, into the structure of which enters the anion $CoCl_5^{---}$, as demonstrated by X-ray investigations [6].

For the purpose of further study of the dependence of this maximum on the concentration, a series of solutions was prepared with a total concentration of 0.15 mole. Measurements of the optical densities of these solutions revealed the presence at $\lambda = 725$ mμ of a maximum corresponding to the complex CoI_4^{--} (Table 5 and Fig. 5). Thus, dilution of the solution from 0.3 molar to 0.15 molar leads to dissociation of the CoI_5 complexes to such an extent that they exert no influence upon the position of the maximum on the optical density/composition curve at $\lambda = 725$ mμ in solutions with a total concentration of 0.15 mole.

Table 5

Optical Densities of Solutions of Cobalt Perchlorate in Presence of Lithium Iodide in Butyl Alcohol

Expt. No.	Composition of solution (in ml)		(in mole/l.)		Optical density at λ (in mμ)						D at λ (in mμ)					
	Co(ClO₄)₂	LiI	Co(ClO₄)₂	LiI	600	625	650	675	700	725	600	625	650	675	700	725
1	4.5	0.5	0.135	0.015	0.068	0.055	0.049	0.033	0.021	0.012	0.003	0	-0.001	-0.003	-0.003	-0.003
	4.5	0	0.135	-	0.065	0.055	0.050	0.036	0.024	0.015						
2	4.0	1.0	0.120	0.030	0.068	0.053	0.050	0.034	0.022	0.012	0.011	0.005	0.006	0.002	0.001	-0.002
	4.0	0	0.120	-	0.057	0.048	0.044	0.032	0.021	0.014						
3	3.5	1.5	0.105	0.045	0.075	0.060	0.060	0.043	0.001	0.015	0.025	0.019	0.023	0.016	0.014	0.020
	3.5	0	0.106	-	0.050	0.041	0.037	0.027	0.017	0.012						
4	3.0	2.0	0.090	0.060	0.087	0.076	0.080	0.065	0.052	0.028	0.045	0.043	0.050	0.043	0.036	0.020
	3.0	0	0.090	-	0.042	0.035	0.030	0.022	0.016	0.008						
5	2.5	2.5	0.075	0.075	0.107	0.104	0.113	0.096	0.080	0.043	0.072	0.075	0.087	0.072	0.066	0.036
	2.5	0	0.075	-	0.035	0.029	0.026	0.018	0.014	0.007						
6	2.0	3.0	0.060	0.090	0.128	0.132	0.154	0.134	0.118	0.065	0.099	0.108	0.133	0.119	0.106	0.069
	2.0	0	0.060	-	0.029	0.024	0.021	0.015	0.012	0.006						
7	1.5	3.5	0.045	0.105	0.147	0.165	0.201	0.180	0.166	0.102	0.126	0.148	0.185	0.168	0.159	0.098
	1.5	0	0.045	-	0.021	0.017	0.016	0.012	0.007	0.004						
8	1.0	4.0	0.030	0.120	0.165	0.182	0.243	0.223	0.208	0.132	0.151	0.170	0.22	0.215	0.203	0.128
	1.0	0	0.030	-	0.014	0.012	0.011	0.008	0.005	0.004						
9	0.5	4.5	0.015	0.135	0.138	0.168	0.218	0.206	0.190	0.128	0.131	0.162	0.212	0.202	0.193	0.126
	0.5	0	0.015	-	0.007	0.006	0.006	0.004	0.003	0.002						

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SUMMARY

1. Solutions of $Co(ClO_4)_2$ + LiCl; $Co(ClO_4)_2$ + LiBr; and $Co(ClO_4)_2$ + LiI in butyl alcohol were investigated by the spectrophotometric technique of physico-chemical analysis.

2. The presence of $CoCl_4^{--}$ complexes was established in a solution of $Co(ClO_4)_2$ + LiCl in butyl alcohol with a total concentration of 0.05 mole.

3. The presence of $CoBr_4^{--}$ complexes was established in a solution of $Co(ClO_4)_2$ + LiBr in butyl alcohol with a total concentration of 0.05.

4. The presence of complexes of CoI_4^{--} was established in solutions of $Co(ClO_4)_2$ + LiI in butyl alcohol with a total concentration of 0.15 mole.

5. The presence of complexes of CoI_4^{--} and CoI_5^{---} was established in solutions of $Co(ClO_4)_2$ + LiI in butyl alcohol with a total concentration of 0.3 mole.

6. The absorption of cobalt (II) – iodide complexes with a higher iodine content is displaced into the long-wave region of the spectrum.

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DEPENDENCE OF THE REDOX POTENTIAL OF BROMIDE-BROMATE MIXTURES

## ON THE CONCENTRATION OF HYDROCHLORIC ACID

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During titration with bromate as reducing agent we found that the oxida-tion-reduction potential falls [1] at the equivalent point of the reaction with increasing acid concentration. One of the possible explanations of this phenomen-on is that with increasing acid concentration the oxidation of the reducing agent takes place at the expense of the bromine evolved during reaction of bromate with the bromide formed in the initial stage of the reaction.

Nevertheless, it appears desirable to undertake a study of the dependence of the oxidation-reduction potential of bromide-bromate mixtures on the concen-tration of hydrochloric acid, since in most cases both direct titration with bromate and oxidation with excess of bromate are carried out in a hydrochloric acid medium.

The normal oxidation-reduction potentials of the systems bromate-bromine, bromine-bromide, and bromate-bromide have been determined with great care by a number of authors [2]. These data, however, do not provide any evidence as to the possible changes in potential during change of acid concentration, particularly in presence of hydrochloric acid. Moreover, the experimental conditions of prev-ious workers differed considerably from those applied when using bromate in volu-metric analysis. Thus, for example, the normal potential of the system bromate-bromine has been determined for the equilibrium state of bromate-saturated bromine solution; that of the system bromine-bromide has been determined for the equilib-ria: liquid bromine-bromide, saturated bromine solution-bromide, and gaseous brom-ine-bromide.

During titration with bromate, bromine ions are formed at the very start of the reaction, so that the following intermediate reaction is unavoidable:

$$BrO_3^- + 5Br^- + 6H^+ \rightleftarrows 3Br_2 + 3H_2O, \qquad (I)$$
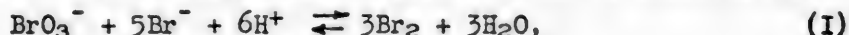
and three equilibria must therefore be considered:

$$2BrO_3^- + 10\underline{e} + 12H^+ \rightleftarrows Br_2 + 6H_2O, \qquad (A)$$

$$BrO_3^- + 6\underline{e} + 6H^+ \rightleftarrows Br^- + 3H_2O, \qquad (B)$$

$$Br_2 + 2\underline{e} \rightleftarrows 2Br^-. \qquad (C)$$

It has been shown by Sammet [2] that the oxidation-reduction potentials of the systems (A), (B), and (C), which are represented by the equations:

$$E_A = E_{OA} + \frac{RT}{10F} \ln \frac{[BrO_3^-]^2[H^+]^{12}}{[Br_2]} ,$$

$$E_B = E_{OB} + \frac{RT}{6F} \ln \frac{[BrO_3^-][H^+]^6}{[Br^-]} ,$$

$$E_C = E_{OC} + \frac{RT}{2F} \ln \frac{[Br_2]}{[Br^-]^2} \, ,$$

are correlated at the equilibrium position of all of the three components of reaction (I) by the expressions:

(1) $E_{OB} - E_{OA} = \frac{RT}{30F} \ln K$, (2) $E_{OC} - E_{OB} = \frac{RT}{6F} \ln K$, (3) $E_{OC} - E_{OA} = \frac{RT}{5F} \ln K$,

where K is the equilibrium constant of reaction (I).

Having determined E_{OC} and E_{OA}, Sammet obtained the value of K = 0.73 = 0.73($\pm$0.21)$\cdot 10^{33}$, from equation (3). This value of the constant shows that with sufficiently high acid concentration the reaction bromate — bromide proceeds to completion with substantially complete removal from the sphere of the reaction of one of the two components of the mixture.

Measurement of the Potential of Mixtures with Excess of Bromide

The measuring procedure was as follows: solutions of $KBrO_3$ of exactly 0.05 and 0.005 molar concentration were prepared, and also solutions of KBr of the same concentrations. These solutions were mixed in such proportions that after addition of hydrochloric acid two series of solutions were obtained, containing bromine and bromine ion: 1) with $[Br_2]$ = 0.005 molar and with $[Br^-]$ = 0.01 molar, and 2) with $[Br_2]$ = = 0.0005 molar and with $[Br^-]$ = 0.001 molar. The reaction was carried out in the very same vessel in which the oxidation-reduction potential was subsequently measured (see drawing).
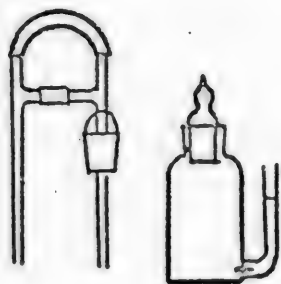
The vessel consists of a small cylindrical bottle of 38-40 ml capacity with a platinum electrode sealed into the side tube. The stopper of the bottle is of ground glass. The volume of reaction mixture was so selected that it filled the vessel almost completely, thus avoiding appreciable volatilization of bromine from the solution. The mixture was rapidly shaken and the bottle closed with the stopper. Potential measurements were performed within 24 hours after the start of the reaction between the components of the mixture; after this period, as shown in control tests, equilibrium has been established and the potential remained constant after more prolonged standing. The following chain was constituted for measuring the oxidation-reduction potential.

$$\left| Pt \right| Br_2, \ Br^- \left| mMHCl \right| HCl = M \left| H_2 \right| Pt \right|.$$
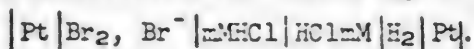
In order to prevent the development of a diffusion potential at the boundary of both half-elements, the concentration of hydrochloric acid in the vessel for measuring the redox potential and in the hydrogen electrode was identical. The electrolytic bridge and the connecting vessel were filled with acid of exactly the same molarity. We prepared the acid for the hydrogen electrode, the electrolytic bridge, and the connecting vessel in the following manner: To the same volume of acid that was introduced into the vessel with the bromate-bromide mixture was added a standard solution of potassium hydroxide in quantity equivalent to the quantity of acid consumed during the reaction of the bromate with the bromide. Thereupon the volume was made up with water to the very same volume that was occupied by the solution under investigation. A batch of this solution large enough for all of the parallel experiments was prepared and its molarity was determined by titration. In order to check whether the activity of the hydrogen ions was the same in both half-elements, the pH values of the hydrogen electrodes were measured in a series of solutions connected to a saturated calomel electrode, and other measurements were made in corresponding solutions, which had contained the system $Br_2 - 2Br^-$, with the aid of the glass electrode after the redox potential of these had been determined. Good agreement was obtained in nearly all cases. Results are given

in Table 1. In the fourth column the pH values calculated from the hydrochloric acid activity on the basis of Linhart's data [3] are shown for comparison.

All of the measurements were performed in a thermostat at 30°. Before the vessel used for measurement of the redox potential was place in the thermostat, its ground glass stopper was rapidly replaced by an electrolytic bridge, one of the limbs of which was sealed into a similar ground glass stopper.

TABLE 1

Molarity of HCl	pH		
	By hydrogen electrode	By glass electrode	Calculated from activity of HCl
0.0458	1.38	1.41	1.37
0.0803	1.11	1.08	1.17
0.1822	0.73	0.82	0.81
0.2211	0.74	0.71	0.77
0.3562	0.51	0.55	0.56
0.5082	0.29	0.44	0.40
0.6493	0.23	0.26	0.30
0.8604	0.12	0.14	0.16
1.0177	0.11	0.01	0.07
1.2300	0.00	-0.07	-0.02
1.2592	-0.07	-0.11	-0.04
1.7935	–	-0.26	-0.25
2.4735	-0.42	-0.46	-0.46
3.7496	-0.73	-0.72	-0.80

The potential of the system $Br_2 + 2e \rightleftharpoons 2Br^-$ is represented by the equation:

$$E_{Br_2/2Br^-} = E_0 + 0.030 \log \frac{a_1^{\frac{1}{2}}}{a_2} =$$
$$= E_0 + 0.030 \log \frac{\gamma_1^{\frac{1}{2}}}{\gamma_2^2} + 0.030 \log \frac{c_1^{\frac{1}{2}}}{c_2^2},$$

where a_1 is the activity, γ_1 is the activity coefficient, and c_1 is the concentration of bromine; a_2 is the activity, γ_2 is the activity coefficient, and c_2 is the concentration of bromine ion. On measuring the emf of the chain constituted according to the scheme given on p. 2024, we obtain:

$$E_{meas.} = E_{Br_2/2Br^-} - 0.060 \log a_H = E_{0Br_2/2Br^-} + 0.030 \log \frac{\gamma_1^{\frac{1}{2}}}{\gamma_2^2} +$$
$$+ 0.030 \log \frac{c_1^{\frac{1}{2}}}{c_2^2} + 0.060 \text{ pH}.$$

Denoting $E_0 + 0.030 \log \frac{\gamma_1^{\frac{1}{2}}}{\gamma_2^2}$ by E_0' (the "apparent" normal oxidation-reduction potential) we find:

$$E_{0Br_2/2Br^-}' = E_{meas.} - 0.030 \log \frac{c_1^{\frac{1}{2}}}{c_2^2} - 0.060 \text{ pH}$$

when $C_1 = 5 \cdot 10^{-3}$ mole and $C_2 = 1 \cdot 10^{-2}$ mole, $0.030 \log \frac{c_1^{\frac{1}{2}}}{c_2^2} = 0.051$

and $E_{0Br_2/2Br^-}' = E_{meas.} - 0.051 - 0.060 \text{ pH}$ (4)

when $C_1 = 5 \cdot 10^{-4}$ mole and $C_2 = 1 \cdot 10^{-3}$ mole, $0.030 \log \frac{c_1^{\frac{1}{2}}}{c_2^2} = 0.081$

and $E_{0Br_2/2Br^-}' = E_{meas.} - 0.081 - 0.060 \text{ pH}.$ (5)

In Table 2 are given the results of measurements of the potential of the system $Br_2 + 2e \rightleftharpoons 2Br^-$, carried out in solutions with $C_1 = 5 \cdot 10^{-3}$ mole and $C_2 = 1 \cdot 10^{-2}$ mole; in the fourth column are the values of $E_{0Br_2/2Br^-}$ calculated from equation (4). All of the results are the mean of several values differing from each other by 2-3 mV.

In Table 3 are presented the results of measurements of the potential of the same system for $C_1 = 5 \cdot 10^{-4}$ mole and $C_2 = 1 \cdot 10^{-3}$ mole; $E_{0Br_2/2Br^-}$ was calculated from Equation (5).

These two tables show that the value of the "apparent" normal oxidation-reduction potential of the system $Br_2 + 2e \rightleftharpoons 2Br^-$, and consequently also the magnitude of $0.030 \log \frac{\gamma_1^{\frac{1}{2}}}{\gamma_2^2}$ at first increases with increasing concentration of hydrochloric

TABLE 2

Molarity of HCl	pH	Emeas.	$E'_{0}Br_2/2Br$
0.0362	1.53	1.206	1.06$_3$
0.0894	1.12	1.200	1.08$_2$
0.1747	0.84	1.188	1.08$_7$
0.2211	0.77	1.191	1.09$_4$
0.3595	0.55	1.177	1.09$_3$
0.5111	0.40	1.160	1.08$_5$
0.6595	0.29	1.144	1.07$_6$
0.8604	0.16	1.135	1.07$_4$
1.0177	0.07	1.123	1.06$_8$
1.2592	-0.04	1.115	1.06$_8$
1.7904	-0.25	1.094	1.05$_8$
2.5286	-0.48	1.066	1.04$_4$
3.7496	-0.80	1.045	1.04$_2$

Heading: $[Br_2] = 5 \cdot 10^{-3}$ mole. $[Br^-] = 1 \cdot 10^{-2}$ mole

TABLE 3

Molarity of HCl	pH	Emeas.	$E'_{0}Br_2/2Br$
0.0458	1.37	1.211	1.04$_8$
0.0918	1.12	1.207	1.05$_9$
0.1713	0.85	1.201	1.06$_9$
0.2234	0.76	1.198	1.07$_2$
0.3551	0.57	1.186	1.07$_1$
0.5082	0.40	1.174	1.06$_9$
0.6493	0.30	1.165	1.06$_8$
0.8762	0.15	1.150	1.06$_0$
1.0216	0.07	1.145	1.06$_0$
1.2300	0.00	1.134	1.05$_4$
1.7613	-0.24	1.116	1.04$_9$
2.4735	-0.46	1.086	1.03$_3$
3.7630	-0.80	1.047	1.01$_4$

Heading: $[Br_2] = 5 \cdot 10^{-4}$ mole. $[Br^-] = 1 \cdot 10^{-3}$ mole

acid and then falls. A consideration of the factors capable of influencing the activity coefficients of bromine and bromine ion during increase in the concentration of hydrochloric acid suggests that the following are concerned: 1) the increase in the ionic strength of the solution; 2) the presence in the solution of the equilibrium $Br_2 + Cl^- \rightleftarrows Br_2Cl^-$; and 3) the existence of the equilibrium $Br_2 + Br^- \rightleftarrows Br_3^-$.

Influence of the Magnitude of the Ionic Strength of the Solution

There are no data in the literature about the influence of this factor upon the activity coefficient of bromine; regarding the activity coefficient of the bromine ion, this falls with increasing ionic strength of the solution, according to the data of Lewis and Randall [4], to a value of $\mu = 0.1$.

Influence of the Equilibrium $Br_2 + Cl^- \rightleftarrows Br_2Cl^-$

It is obvious that displacement of the equilibrium $Br_2 + Cl^- \rightleftarrows Br_2Cl^-$ to the right must reduce the activity coefficient of bromine. Jakowkin [5] found,

$K = \dfrac{[Br_2][Cl^-]}{[Br_2Cl^-]}$, values in the range of 0.69-0.76. This constant, however, is equal to 0.708 according to Ray and Sarkar [6].

Influence of the Equilibrium $Br_2 + Br^- \rightleftarrows Br_3^-$

This equilibrium is bound to have an effect both upon the activity coefficient of bromine and that of bromine ion. Jakowkin [7] found that

$K = \dfrac{[Br_2][KBr]}{[KBr_3]} = 0.063$ (0.061-0.066); similar results were obtained by Lewis and Storch [2]; Griffith, McKeown, and Winn [8] obtained approximately the same values for the equilibrium constant, and according to their data K increases with increasing ionic strength of the solution.

Nevertheless, the foregoing equilibrium can scarcely be expected to exercise a great influence upon the magnitude of 0.030 log γ_1/γ_2^2, since if the activity of Br_2 increased in consequence of the formation of Br_3^-, then the activity coefficient of Br^- should be correspondingly reduced. Lewis and Randall [9] consider that the activity coefficient of Br_3^- is 8% smaller than the activity coefficient of Br^-. Hence, the chief factor influencing the magnitude of the "apparent" normal oxidation-reduction potential of the system $Br_2 + 2e \rightleftarrows 2Br^-$ on increase of concentration of hydrochloric acid may be assumed to be the equilibrium $Br_2 + Cl^- \rightleftarrows Br_2Cl^-$.
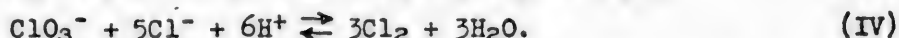
The pH values in this table and the later tables are calculated from the values of the activity of HCl.

Measurement of Redox Potential in Solutions of Mixtures with Excess of Bromate

In practice such mixtures are formed during the oxidation of reducing agents with excess of bromate. In a hydrochloric acid medium in presence of an excess of bromate the reactions:

$$BrO_3^- + 5Br^- + 6H^+ \rightleftarrows 3Br_2 + 3H_2O; \quad Br_2 + Cl^- \rightleftarrows Br_2Cl^-, \tag{I}$$

may be accompanied by the reactions:

$$2BrO_3^- + 10Cl^- + 12H^+ \rightleftarrows Br_2 + 5Cl_2 + 6H_2O, \tag{II}$$

$$6BrO_3^- + 5Cl^- + 6H^+ \rightleftarrows 3Br_2 + 5ClO_3^- + 3H_2O, \tag{III}$$

$$ClO_3^- + 5Cl^- + 6H^+ \rightleftarrows 3Cl_2 + 3H_2O. \tag{IV}$$
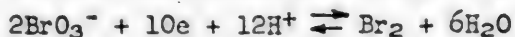
The hydrochloric acid concentration at which reaction (II) commences was established as approximately 0.2 molar for a BrO_3^- concentration of 0.001 molar. The following procedure was used for determination of the foregoing hydrochloric acid concentration. Into flasks with ground glass stoppers were introduced 1 ml of a 0.02 molar solution of $KBrO_3$ and 20 ml of hydrochloric acid of varying concentration; a small piece of paper moistened with indigo carmine was suspended in the flask and then the flask was tightly closed. At hydrochloric acid concentrations of 0.17 and 0.22 molar decolorization of the edges of the paper was observed only after 24 hours; at a hydrochloric acid concentration of 0.35 molar, decolorization of the paper set in rapidly. In precisely the same manner the minimum concentration of acid required for initiation of reaction (IV) was established. After 24 hours traces of chlorine were detected at hydrochloric acid concentrations of 0.88 molar and 1.08 molar; at a HCl concentration of 1.25 molar and higher, appreciable decolorization of the indigo carmine was observed only after 24 hours.

For confirmation of formation of chlorate ion in a hydrochloric acid solution of bromate-bromide mixture on prolonged standing, we applied the method of Fichter and Tschudin [10] for quantitative determination of bromates in presence of chlorates. The basis of the method is that the reaction between bromate ions and iodine ions proceeds almost instantaneously, whereas that between chlorate ions and iodine ions proceeds extraordinarily slowly. In our case bromate ions participate in the reaction with iodine ions (if not all of the bromate has decomposed towards the end of the reaction), as well as free bromine and free chlorine; consequently the difference between the quantity of bromate taken and that found after reaction with hydrochloric acid should correspond to the amount of chlorate formed. Into a flask with a ground glass stopper were measured various amounts of bromate and hydrochloric acid; after standing for 24 hours, the sum of the bromate, bromine and chlorine was determined iodometrically. Results are shown in Table 4. In Expt. 3 the solution was diluted twice before the addition of potassium iodide; in Expt. 4 it was diluted 4 times.

TABLE 4

Expt. No.	Volume of HCl (ml)	Molarity of the KBrO₃	Volume of KBrO₃ (ml)	Amount of KBrO₃ taken, g	Amount of KBrO₃ found, g	Note
1	20	0.15	1.00	0.0027	0.0021	In the last column
2	20	0.37	1.00	0.0027	0.0018	the amount of KBrO₃
3	40	0.50	10.00	0.0283	0.0208	comprises the sum of
4	40	2.50	10.00	0.0283	0.0158	KBrO₃, Br₂ and Cl₂, computed as KBrO₃

The slowness of reaction (III) is demonstrated by the fact that bromate in hydrochloric acid solutions can be quantitatively determined with great accuracy. The low speed of this reaction may be explained by the fact that there is a very slight difference between the oxidation-reduction potentials of the systems:

$$2BrO_3^- + 10\underline{e} + 12H^+ \rightleftarrows Br_2 + 6H_2O$$

$$\text{and} \quad ClO_3^- + 6\underline{e} + 6H^+ \rightleftarrows Cl^- + 3H_2O.$$

The normal oxidation-reduction potentials are $E_{0 BrO_3^-/\frac{1}{2} Br_2} = 1.50$ V and $E_{0 ClO_3^-/Cl^-} = 1.44$ V. The equilibrium constant of the reaction, according to these data, is 10^{30} (at 30°).

From the foregoing observations it follows that the following systems must be present in hydrochloric acid solutions of bromate-bromide mixtures with an excess of bromate: bromate-bromine, chlorine-chlorine ion, chlorate-chlorine ion, and chlorate-chlorine, their amounts depending upon the hydrochloric acid concentration.

The nature of the changes of redox potential of solutions of this type was studied by the same method as for the system $Br_2 + 2\underline{e} \rightleftarrows 2Br^-$. The initial solutions of bromate and bromide were mixed in the ratio of 7:5 and diluted fivefold with solutions of hydrochloric acid; the reaction mixture was left for 24 hours and then the oxidation-reduction potential was measured. Results for two series of solutions are presented in Tables 5 and 6.

TABLE 5				TABLE 6			
Initial conc. of $KBrO_3$ and KBr = 0.05 molar				Initial conc. of $KBrO_3$ and KBr = 0.005 molar			
Molarity of HCl	pH	$E_{meas.}$	Redox potential	Molarity of HCl	pH	$E_{meas.}$	Redox potential
0.0362	1.53	1.361	1.26_9	0.0458	1.37	1.352	1.27_0
0.0894	1.12	1.381	1.31_4	0.0913	1.12	1.368	1.30_1
0.1747	0.84	1.407	1.35_5	0.1822	0 81	1.377	1.32_8
0.2211	0.77	1.411	1.36_5	0.2234	0.76	1.383	1.33_7
0.3595	0.55	1.401	1.36_8	0.3551	0.57	1.400	1.36_8
0.5111	0.40	1.386	1.36_2	0.5082	0.40	1.383	1.35_9
0.6595	0.29	1.369	1.35_2	0.6493	0.30	1.373	1.35_5
0.8604	0.16	1.342	1.33_2	0.8762	0.15	1.354	1.34_5
1.0177	0.07	1.338	1.33_4	1.0216	0.07	1.322	1.31_8
1.2592	-0.04	1.325	1.32_7	1.2300	0.00	1.295	1.29_7
1.7804	-0.25	1.297	1.31_2	1.7613	-0.24	1.266	1.28_0
2.5286	-0.48	1.267	1.29_8	2.4735	-0.46	1.236	1.26_4
3.7496	-0.80	1.225	1.27_3	3.7630	-0.80	1.183	1.23_1

These tables reveal that with increasing concentration of hydrochloric acid from 0.04 to 3.75 molar, the oxidation-reduction potential of the mixture at first rises fairly rapidly up to a concentration of 0.35 mole of hydrochloric acid and thereafter falls gradually.

This influence of the hydrochloric acid concentration may be ascribed to the fact that at low concentrations of hydrochloric acid the system bromate-bromine predominates in the solution, and the potential of this system increases with increasing hydrogen ion concentration. At the same time in the solution there is formed, according to reaction (III), the system chlorate-chlorine ion, the potential of which, on the one hand, must increase with increasing hydrogen ion concentration, and, on the other hand, must fall sharply with increasing concentration of chlorine ions. Finally, at a hydrochloric acid concentration higher than 0.2 molar, the rapid reaction (II) takes place, i.e., the predomina-

ting influence upon the potential of the mixture will be exercised by the system $Cl_2 + 2\underline{e} \rightleftarrows 2Cl^-$.

SUMMARY

1. A study was made of the influence of the hydrochloric acid concentration upon the oxidation-reduction potential of the system $Br_2 + 2\underline{e} \rightleftarrows 2Br^-$ within the concentration range of 0.04-3.75 moles HCl.

2. Up to 0.22 molar concentration of HCl the potential was found to increase, and subsequently to fall.

3. The cause of the fall in the redox potential is the reaction $Br_2 + Cl^- \rightleftarrows Br_2Cl^-$.

4. The reactions taking place in hydrochloric acid solutions in bromate – bromide mixtures containing excess of bromate were investigated.

5. The oxidation-reduction potential of bromate – bromide mixtures containing excess of bromate was studied in dependence on the hydrochloric acid concentration in the range of 0.04 to 3.75 moles HCl.

6. The potential is found to increase with increase of hydrochloric acid concentration to 0.35 molar, and then falls.

7. The cause of the fall in the redox potential is the predominance in strong hydrochloric acid solutions of the system $Cl_2 + 2\underline{e} \rightleftarrows 2Cl^-$.

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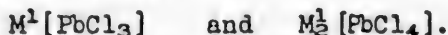
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LEAD CHLORIDE COMPLEXES

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Two formulas are ascribed in most cases to the lead chloride complexes existing in aqueous solutions:

$$M^1[PbCl_3] \quad \text{and} \quad M^1_2[PbCl_4].$$

It is perfectly natural to assume that a mobile thermodynamic equilibrium exists between complex ions of various compositions, and that the position of the equilibrium will depend upon the concentration of chlorine ions in the solution

$$PbCl_4^{--} \rightleftarrows PbCl_3^- + Cl^-.$$

Moreover, with decreasing content of chlorine ions, the $PbCl_3^-$ ion can undergo more far-reaching dissociation in accordance with the equations:

$$PbCl_3^- \rightleftarrows PbCl_2 + Cl^-,$$
$$PbCl_2 \rightleftarrows PbCl^+ + Cl^-,$$
$$PbCl^+ \rightleftarrows Pb^{++} + Cl^-.$$

An increase in the concentration of chlorine ions in the solution will reduce the dissociation and the complex-forming ability of ions of more complex structure.

In the present investigation we have applied the polarographic method to the determination of the ions formed in aqueous solutions containing ions of chlorine and lead in various proportions.

The current strength/voltage curves were plotted with the aid of the visual apparatus [1], with which measurements of diffusion currents can be performed to an accuracy of up to 1 per cent. The electrolyzer consisted of a small spherical vessel provided with an adapter for passing a stream of hydrogen through the analyzed solution. The anode was a saturated calomel half-element which was connected to the electrolyzer by an electrolytic bridge via an intermediate vessel.

Experiments were carried out at constant temperature in a thermostat at $25 \pm 0.2°C$. The capillary had the characteristics:

$$\underline{m} = 1.4 \text{ mg/sec.}, \quad \tau = 3.1 \text{ sec.}$$

For the investigations a whole series of solutions were prepared containing lead nitrate in the constant concentration of 0.004 mole/liter together with increasing quantities of hydrochloric acid. Also to all of the solutions potassium

nitrate was added in 0.1 N concentration. The highest hydrochloric acid concentration used by us was 6.5 N. Further increase in the hydrochloric acid concentration involved the difficulty that in more concentrated solutions the hydrogen wave of the acid was superposed on the diffusion current of lead and hindered a reliable measurement of the half-wave potential.

In our work we used "analytically pure" nitrates and "chemically pure" hydrochloric acid.

During complex formation in solution, the half-wave potential of the metal ions is progressively shifted in the electronegative direction due to the fall in the "active" concentration of the metal in accordance with the relation:

$$(\pi_{1/2})_k - (\pi_{1/2})_2 = \frac{0.058}{n} \log k_c - p \frac{0.058}{n} \log a, \tag{1}$$

which is valid at 25°.

In this equation $(\pi_{1/2})_k$ and $(\pi_{1/2})_2$ are the half-wave potentials of the complex ions and the hydrated ions of the metal; k_c is the instability constant of the complex ions; p is the coordination number; n is the valency of the metal ions, and a the activity of the ions which form complexes with the metal ions. By means of equation (1) the coordination number of the complex and its instability constant can be computed.

But equation (1) can only be applied for these purposes if the rate of dissociation of the complex ions does not limit the reactions at the electrode and if the diffusion current is uninfluenced by the concentration of chlorine ions in the solution.

Our experiments have established that with increasing hydrochloric acid concentration the half-wave potential of lead is shifted approximately from -0.4 to -0.6 V with an increase in acid content from 0.025 to 6.5 moles/liter. At the same time the diffusion current of lead remains constant and uninfluenced by the activity of the hydrochloric acid in solution. The following expression can be readily derived from equation (1):

$$\frac{d\pi_{1/2}}{d \log a} = - p \frac{0.058}{n} . \tag{2}$$

We determine the magnitude of n with the well-known equation for the polarographic wave:

$$\pi = \pi_{1/2} + \frac{0.058}{n} \log \frac{i_d - i}{i} , \tag{3}$$

where π is the potential of the mercury electrode, and i is the current at a given value of the potential of the dropping mercury electrode.

The experimental plots of π versus $\log \frac{i_d - i}{i}$ when the process at the electrode is reversible must yield a straight line from the slope of which can be calculated the valency of the ions of the metal or the number of electrons participating in the process of reduction. In our case, for a large number of measurements, this value proves to be equal to 2, which is in good agreement with the theoretical value for the divalent ion of lead.

The experimental data are represented graphically as a plot of $\pi_{1/2}$ versus $\log a_{HCl}$.

The graph shows that at hydrochloric acid concentrations greater than 3.0 moles/liter a complex anion of the composition $[PbCl_4]^{--}$, is present in the solution; with progressive decrease in the acid concentration the complex undergoes changes in structure so that at acid concentrations of 0.8 to 2.5 moles/liter the anion of the composition $[PbCl_3]^-$ predominates. With further fall in the activity

of the hydrochloric acid, the composition of the anions undergoes further simplification. Consequently, the experimental data confirm the existence in the solution of an equilibrium between complex anions of lead, the decomposition of which proceeds stepwise, as is usual with polyvalent compounds. In respect of hydrochloric acid solutions with a concentration of 3.0 to 6.5 moles/liter the following relation exists between the half-wave potentials of the dropping mercury electrode and the activity of the acid:

$$\pi_{1/2} = -0.446 - 0.112 \log a_{HCl}. \quad (4)$$

Dependence of the half-wave potential of lead on the logarithm of the activity of hydrochloric acid.

Taking the value of 0.4 V for $\pi_{1/2}$ in the case of hydrated ions of lead, as measured under our conditions, we obtain a value of $k_c = 2.5 \cdot 10^{-2}$ for the instability constant of the $[PbCl_4]^{--}$ ion. For the complex of the composition $[PbCl_3]^-$ the slightly lower value of $2 \cdot 10^{-2}$ is obtained. These values are in satisfactory agreement with those of Korenmann [2] and indicate the approximately equal stabilities of the lead chloride complexes.

In a series of experiments we examined the influence of temperature upon the magnitude of the half-wave potential of the ions of lead chloride complexes. It was found that within the limits of accuracy of our measurements ($\pm$ 0.005 V) the half-wave potential of lead remains constant over the temperature range of 0 to 40°.

SUMMARY

1. The reduction of lead ions at the dropping mercury electrode from hydrochloric acid solutions of various concentrations is found to proceed reversibly.

2. The coordination numbers of the resultant lead-chlorine complex ions are found from the displacement of the half-wave potential of lead with change in the activity of hydrochloric acid.

3. In solutions containing lead chloride complexes, an equilibrium is established between the latter, the position of which is governed by the activity of the hydrochloric acid.

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POLAROGRAPHIC DETERMINATION OF SOME ELECTROLYTIC CHARACTERISTICS OF

ZINC IONS

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Thanks to its speed and accuracy the polarographic method of determination of electrochemical characteristics has become a most important electrochemical method. The results of studies by the school of Academician Frumkin [1] and others [2], aiming at clarification of the dependency of the magnitude of the diffusion current upon the nature and concentration of the so-called indifferent electrolyte, enable this method to be applied to the determination of transference numbers, mobilities, and diffusion coefficients of ions by the measurement of the diffusion current [3].

The magnitudes of the mobilities and diffusion coefficients of ions of metals provide a basis for calculation of the velocity of electrolysis of salts, since these characteristics are the most important factors governing the velocity. Ions migrate toward an electrode in solution by overcoming the resistance of the medium, and when they are subjected to a constant current strength (tension of the electric field) their migration velocity is directly proportional to this current strength and inversely proportional to the size of the moving particles. In this connection attempts to apply Stokes' law have been made in recent years [5,6]. It has been found that the smaller the radius of the ion for one and the same electric charge, the greater its tendency to combine with molecules of the solvent, i.e., the greater becomes the radius of the solvated ion. The degree of solvation of ions decreases with increasing complex-forming activity of the solvent.

With the objective of studying the behavior of zinc ions in simple and buffered solutions, we carried out experiments on the determination of the transference numbers, mobilities (U_i), and diffusion coefficients (D_i) of these ions, and also experiments on the effect of the concentration of zinc sulfate on these characteristics by the polarographic method. In addition, a study was made of the influence of the concentration of potassium chloride, sodium tartrate, and sodium citrate, and of the pH of the medium on the velocity of migration and diffusion of these ions in course of their electrolysis.

The original theory of Arrhenius, stating that the transference numbers do not depend upon the concentration of the electrolytes, postulated that the mobility of ions does not change with change in their concentration. Debye established that the rate of ionic velocity depends on their concentration, an increase in concentration resulting in a fall in the rate of ionic movement [4]. The higher the electric conductivity of electrolytes the higher is the mobility of their ions. If we know the transference numbers of the ions of a given electrolyte and its limiting conductivity in solution, then from the formulas

$$\underline{v} = \underline{n}\lambda_0 \quad \text{and} \quad \underline{u} = (1 - \underline{n})\lambda_0,$$

we can calculate the mobility of the ions of the same electrolyte. Determination of the transference numbers and mobility of ions by the classical methods calls for skilful and careful manipulation which renders the operation laborious and

consumes considerable time [5], whereas measurement of the limiting and diffusion current with the direct-reading polarograph is not particularly laborious and requires not more than 10-15 minutes. Another drawback of the classical method is that the ionic mobility cannot be determined in all media by means of it.

The recording of the polarogram also provides information, on the basis of the change in deposition potentials of the metals, about the presence or absence of complex ions in the solutions under investigation.

EXPERIMENTAL

Since there is no possibility of a polarizing action of metals during electro-deposition when working with the constantly renewed, fresh and active surface of the dropping mercury cathode, all phenomena testifying to a fall in the velocity of electrodeposition of the metals must be ascribed to polarizing actions coming into play in the solution, such as retarded arrival of ions at the electrode, retarded detachment of simple ions from complex ions. Ions arrive at the surface of the cathode as a result of: 1) a diffusive force proportional to the concentration gradient between the solution at the cathode surface and the main bulk of solution; and 2) an electric force proportional to the gradient of the electric potential in the vicinity of the mercury cathode. But in presence of an excess of indifferent electrolyte the electric migration of the ions which are being reduced is inhibited and such ions will only arrive at the cathode under the influence of diffusion. On the basis of these considerations, Ilkovic [7] used the following theoretically derived formula for calculation of the strength of the diffusion current:

$$i_d = 605 \ ncD^{1/2}m^{2/3}t^{1/6}, \tag{1}$$

where i_d = diffusion current expressed in μA;
  c = concentration of electrolyte in millimoles per liter;
  D = diffusion coefficient in $cm^2/sec.$;
  t = time of outflow of a drop in seconds;
  m = amount of mercury in mg flowing from the capillary per second.

Hence, the effective diffusion coefficient is:

$$D = \frac{i^2_d}{(605 \ ncm^{2/3}t^{1/6})^2}. \tag{2}$$

According to Nernst [8], however, the diffusion coefficient is given by:

$$D = \frac{RT}{nF^2} \ U_1, \tag{3}$$

where R is the gas constant; T is the absolute temperature; n is the valency; F is the number of farads; U_1 is the ionic mobility, $= U_1F$; and U_{o1} is the absolute velocity of ionic movement.

Substituting the ionic mobility in the Nernst formula by this magnitude, and equating equation (2) with equation (3), we obtain a formula from which, knowing the magnitude of the diffusion current i_d, we can calculate the absolute velocity of the ions:

$$U_{o1} = 1.08 \cdot 10^{-4} \ \frac{i^2_d}{c^2k^2n}, \tag{4}$$

where
$$k = m^{2/3}t^{1/6}.$$

The zinc sulfate used for determination of the values of U_{o1} and D_1 of zinc ions was a twice recrystallized Kahlbaum preparation. The titer of the starting solution was established triply by the method of Tamm [9]; the mean

value of $T_{Zn} = 0.0006535$ g (0.01 mole).

The indifferent electrolyte, potassium chloride, was recrystallized three times. Buffer solutions were prepared from Kahlbaum's sodium tartrate and sodium citrate. Measurements were effected on the direct-reading polarograph of the Chemical Research Institute of Gorky State University; the galvanometer was of the type designed by the Leningrad Institute of Physical Apparatus Construction. Its absolute sensitivity was $3.2 \cdot 10^{-9}$ A/mm, $R_{int.} = 200$ ohm; $R_{total} = 400$ ohm. $T = 4.8$ sec. Use was also made of the Odessa M 8 automatic polarograph. The drum had a speed of 7 turns/minute. The galvanometer was of the same type with an absolute sensitivity of $1.1 \cdot 10^{-9}$ A/mm. The distance from the center of the mirror to the sensitized drum is 0.8 mm. $R_{int.} = 850$ ohm. $R_{total.} = 1158$ ohm. $T = 5.4$ sec. A 4-volt accumulator was used. The electrolyzed solution had a volume of 10-15 ml; the temperature of the solution was 20°C. $\underline{m}$ was determined at the corresponding decomposition voltage of zinc. The capillary constants used for calculation of D_i and U_{0i} were as follows:

Type of polarograph	$t^{1/2}$ (sec)	$m^{2/3}$ (mg)	$m^{2/3}t^{1/6}$ $mg^{2/3}$ sec.$^{-2}$
Direct reading $\{$	2.8	2.5	2.20
	2.8	2.6	2.25
Automatic	3.0	4.1	3.10

The height of the polarographic wave ($\underline{h}$) was determined by Hohn's method. Conversion of the height of wave, measured in millimeters, into strength of diffusion current (μA) was effected with the aid of the formula:

$$i_d = \frac{hab \ 10^6}{1} \ ,$$

where $\underline{a}$ = absolute sensitivity of the galvanometer;
   $\underline{b}$ = coefficient of fall in sensitivity of the galvanometer;
   $\underline{1}$ = distance from center of galvanometer mirror to the sensitized drum or
       to the galvanometer scale.

A study was made of the following factors with a view to determining the transference numbers, diffusion coefficients, and mobilities of the ions of zinc under various conditions by the polarographic method:

1) Dependence of the limiting current on the concentration of zinc sulfate solution and the influence of this concentration on $\underline{U}_{0i}$, $\underline{D}_i$, and the transference numbers of zinc ions.

2) Influence of the potassium chloride concentration upon the $\underline{U}_{0i}$ and $\underline{D}_i$ of zinc ions.

3) Dependence of the values of $\underline{U}_{0i}$ and $\underline{D}_i$ of zinc ions upon the pH and concentration of the tartrate and citrate buffer solutions.

1. Dependence of the Limiting Current upon the Concentration of Zinc Sulfate Solution and the Effect of this Concentration upon the U_{0i}, D_i, and Transference Numbers of Zinc Ions

The dependence of the limiting current on the concentration of the zinc sulfate solution was studied with varying sensitivity of the galvanometer. Figure 1 reveals a rectilinear relation between the concentration of zinc sulfate solution and the limiting current. The limiting current may be regarded as the sum of the migration (i_m) and the diffusion currents (i_d) [10]:

$$i_e = i_m + i_d. \qquad (5)$$

If the solution contains no other substances than those undergoing electrolytic reduction, then the migration current will be equal to that portion of the total of i_e which is transferred by the cations which are being electrodeposited, i.e.:

$$n_c = \frac{i_m}{i_e} = \frac{u}{u + v}. \qquad (6)$$

It follows from equations (5) and (6) that

$$n_a = \frac{i_d}{i_e} = \frac{v}{u + v}.$$

As we know, the number of ions capable of being reduced at the cathode and transferring to the cathode can be rendered infinitely small by introducing into the electrolyte a relatively large excess of indifferent electrolyte. Under these conditions the passage of current through the solution will be effected only by ions of the indifferent electrolyte, and the electrical migration of the ions which are bieng reduced will become negligible: these ions will arrive at the cathode only as a result of diffusion. These conditions were realized by conducting the polarographic reduction in presence of an 0.1 molar solution of KCl.
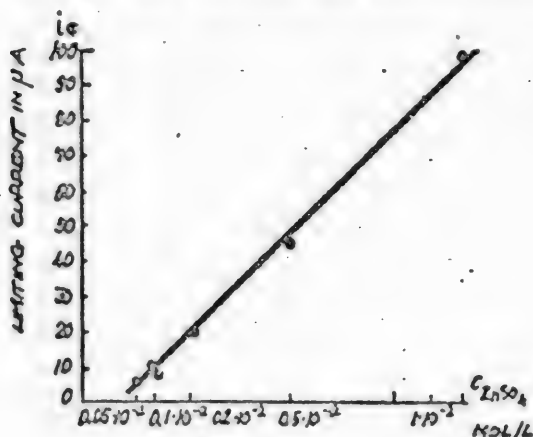
As shown in Table 2, the height of wave in presence of an 0.1 molar solution of KCl (diffusion current) is much below that of the limiting current wave.

A maximum period of 30 minutes is required for determination of the transference numbers by this method, as against not less than 6 hours by the classical method.

As is well known, a most important factor in the electric conductivity of a solution of electrolytes is the ionic

Fig. 1. Dependence of the limiting current on the concentration of zinc sulfate solution.

TABLE 1 ••

Influence of c_{ZnSO_4} on i_{lim}.

Expt. No.	Sensitivity of galvanometer	Concentration of $ZnSO_4$ (moles/l.)	Height of the polarographic wave (in mm)	Limiting current, i_e (μA)	Deposition potential
1	1/150	$1 \cdot 10^{-2}$	55.0	106.0	-1.28
2	1/100	$1 \cdot 10^{-2}$	82.0	105.0	-1.28
3	1/25	$2 \cdot 10^{-3}$	65.5	21.0	-1.29
4	1/25	$1 \cdot 10^{-3}$	33.0	10.6	-1.29
5	1/25	$5 \cdot 10^{-4}$	16.5	5.3	-1.29
6	1/10	$5 \cdot 10^{-5}$	4.5	0.575	-1.29
7	1/150	$1 \cdot 10^{-2}$	51.0	97.5	-1.24
8	1/100	$1 \cdot 10^{-2}$	76.0	97.4	-1.24
9	1/25	$2 \cdot 10^{-3}$	62.5	20.0	-1.25
10	1/25	$1 \cdot 10^{-3}$	31.0	9.9	-1.26
11	1/25	$5 \cdot 10^{-4}$	16.0	5.1	-1.26
12	1/1000	$1 \cdot 10^{-2}$	104.6	144.0	-1.24
13	1/300	$1 \cdot 10^{-3}$	34.4	14.2	-1.26
14	1/500	$2 \cdot 10^{-3}$	44.7	30.6	-1.25
15	1/300	$5 \cdot 10^{-4}$	17.5	7.2	-1.26

n_a and n_k are respectively the transference number of the anion and the cation.
•• See Table 2 next page.

TABLE 2

Influence of c_{ZnSO_4} on the Transference Number of Zn'' and SO_4''

Expt. No.	Height of wave of limiting current (in mm)	Limiting current (i_e) (in μA)	Concentration (in moles/l.)	Height of wave of diffusion current (in mm)	Diffusion current (i_d) (in μA)	Sensitivity of the galvanometer (S)	$n_{SO_4''}$ transference number	$n_{Zn''}$ transference number	$U_{Zn''}$ cm/sec·10^{-4}
1	76.0	97.4	$1 \cdot 10^{-2}$	50.0	64.0	1/100	0.66	0.34	4.57
2	62.5	20.0	$2 \cdot 10^{-3}$	40.0	12.80	1/25	0.64	0.36	4.6
3	44.7	50.6	$2 \cdot 10^{-3}$	134.5	18.45	1/500 and 1/100	0.604	0.39	4.62
4	104.5	144.0	$1 \cdot 10^{-2}$	132.0	90.50	1/1000 and 1/500	0.63	0.37	4.8
5	–	–	$1 \cdot 10^{-3}$	67.0	9.20	1/100	–	–	4.3

Note to Table 1: 1) Experiments 1-6 were performed without addition of methyl orange. 2) Methyl orange was used in experiments 7-15 (2 drops of 0.1 N solution per 15 ml of solution). 3) Measurements in experiments 1-11 were made with the visual polarograph and in experiments 12-15 with the automatic instrument.

Note to Table 2: 1) Visual polarograph used in experiments 1 and 2, automatic polarograph in experiments 3-5, 2) The capillary constant of the direct-reading instrument was 2.2, that of the automatic instrument 3.1. 3) In column 7 the values 1/500 and 1/1000 relate to limiting current, and 1/100 and 1/25 to diffusion current.

mobility, which is characterized by the velocity with which the ions travel through the electrolyzed solution to the cathode. The more rapidly the ions move through the solution the greater the number discharged at the electrodes per unit of time.

The data of Table 2 show that the polarographic determination of the absolute velocity of ionic movement gives satisfactory results; the deviation from the results published in the literature [11] is insignificant and is within the limits of experimental error. As was also to be expected, U_{oi} generally decreases with increasing concentration of $ZnSO_4$. Knowing the transference numbers of this salt and the absolute mobility of zinc ions, we can determine the mobility of its partner under the given conditions:

$$V_{oi} = U_{oi} \cdot \frac{n_{SO_4''}}{n_{Zn''}} = 4.62 \cdot 10^{-4} \cdot \frac{0.604}{0.396} = \sim 7.05 \cdot 10^{-4} \text{ cm/sec.}$$

2. Influence of the Potassium Chloride Concentration upon the Values of U_{oi} and D_i of Zinc Ions

As reported by a whole series of investigators [1,2,12], the strength of the diffusion current of the cation under examination in presence of one and the same indifferent electrolyte, the latter in various concentrations, varies. These fluctuations in the diffusion current are caused, in all probability, by a change in the value of the U_{oi} of the ions with changing concentration of the indifferent electrolyte.

The diffusion coefficients of ions also vary with the nature and concentration of the indifferent electrolyte. Kolthoff and Lingane, in a study of the diffusion of the cadmium ion, detected an increase in its effective diffusion coefficient in the presence of KCl. They explain this phenomenon by the formation of $CdCl'$ which has a greater degree of mobility than Cd'' [2] owing to its lower degree of hydration. To clarify the influence of the KCl concentration on the rate of movement and diffusion of zinc ions, a series of experiments was performed in which the $ZnSO_4$ concentration remained constant. These experiments

revealed that when the concentration of the KCl solution was higher than 0.1 N, the resultant diffusion current exceeded the normal diffusion current. The data of Table 3 (column 4) and Fig. 2 indicate that the height of the polarographic wave in presence of KCl of varying concentration undergoes variations. An increase in the KCl concentration to 0.6 N increases the U_{01} and D_1 of zinc ions, but further increase in the KCl concentration does not lead to further rise in the rate of movement and diffusion of zinc ions; the latter values remain practically constant.
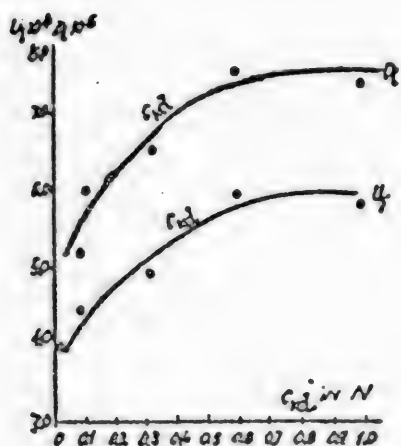
The relatively large increase in the i_d of zinc ions with increasing KCl concentration can only be explained by a change in the effective diffusion coefficient. Since the presence of an excess of KCl within the limits of the abovementioned range in the solution of the electrolyte undergoing reduction does not influence the capillary constant, while c_{ZnSO_4} and n are constant in the present case (formula of Ilkovic), it is evident that i_d is dependent only on D_1 ($i_d =$

Fig. 2. Influence of KCl concentration on U_1 and D_1 of zinc ion.

$= K \cdot D^{1/2}$. It is possible that the ions of zinc undergo desolvation in view of the presence in the solution of an overwhelmingly greater proportion of KCl.

TABLE 3

Expt. No.	KCl concentration, (normality)	Height of polarographic wave (mm)	Diffusion current (i_d) (μA)	U_{01} (cm/sec·10^4)	D_1 (cm^2/sec·10^6)	$m^{2/3}t^{1/6}$ (mg$^{2/3}$·sec$^{-1/2}$)
1	0.15	27.0	18.4	4.70	5.90	3.1
2	0.30	27.5	19.1	5.07	6.21	3.1
3	0.60	28.5	19.7	5.40	6.80	3.1
4	1.00	28.5	19.7	5.40	6.80	3.1
5	0.05	37.5	12.0	4.00	5.19	2.2
6	0.10	40.0	12.8	4.60	5.90	2.2
7	0.30	42.5	13.6	5.10	6.65	2.2
8	0.60	45.0	14.4	5.75	7.45	2.2
9	1.00	45.0	14.4	5.75	7.45	2.2

Note to Table 3: 1) Automatic polarograph used in expts. 1-4, visual instrument in expts. 5-9. 2) Galvanometer sensitivity S=1/25. 3) Conc. of the polarographed ZnSO$_4$ solution = $2 \cdot 10^{-3}$ mole/l.

3. Dependence of U_{01} and D_1 of Zinc Ions on the pH and Concentration of Tartrate and Citrate Buffer

Previously we had observed that in the polarographic analysis of zinc in a citrate-buffered solution at a pH of 4.5 to 8.2, the height of the polarographic wave of zinc falls sharply and the polarographic curve is seriously distorted [13]. On the other hand, the speed of electrodeposition of zinc on a platinum cathode

(at room temperature) is markedly reduced, clearly because of the retardation of ionic movement in a citrate medium with a pH of 6.0 to 8.0. A significant acceleration of zinc electrolysis only occurred when the temperature was raised to 50-80°. The earlier observations were confirmed in more careful studies of the phenomenon of retardation of zinc electrolysis at higher pH values within the ranges indicated.

Thus, the hydrogen ion concentration has a marked influence upon the D_1 and U_{01} of the cations of non-ferrous metals. In particular, D_1 is considerably reduced in solutions in which complexes are formed. The stability of complex ions of metals will vary with the pH of the buffered medium. We made a study of this relation using citrate- and tartrate-buffered solutions, and we present the experimental results in Table 4. These investigations show that with increasing pH the strength of the diffusion current decreases. An examination of the effect of the pH of the medium upon the rate of movement and diffusion of zinc ions showed that at a pH of the citrate-buffered medium greater than 4, the absolute mobility of zinc sharply decreases and becomes nearly constant at a pH of 5 to 7 (Fig. 3). It is known that citrate solutions are favorable media for complex formation of metal ions. Consequently, the fall in U_{01} and D_1 of zinc ions may be correlated

Fig. 3. Dependence of the absolute mobility of zinc ions upon the pH of citrate- and tartrate-buffered solutions.

with the increase in the effective radius of the complex ion of this metal. A pH of 4.4 and higher promotes the formation of a more stable complex ion of zinc, the effective radius of which is accordingly greater than that of a simple zinc ion. Further evidence of the formation of complex ions of zinc in citrate- and tartrate-buffered solutions is provided by the displacement of the reduction potentials of the ions of this metal. As shown in Table 4, the potentials are displaced in the negative direction, starting from a pH approaching 4.4.
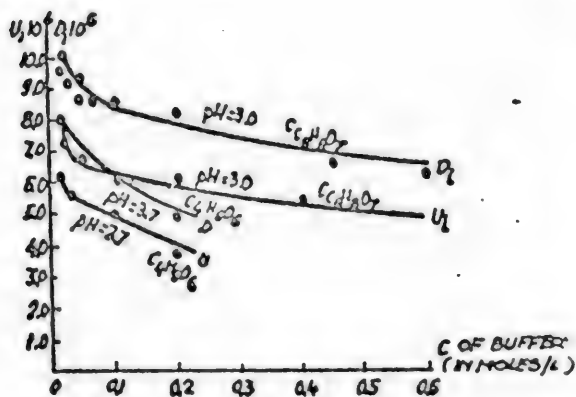
On the basis of these observations (Table 4) it may be concluded that the medium with the most favorable effect upon the mobility and diffusion of zinc ions is an acid medium with a pH of 2.0 to 4.5 for the citrate-buffered solution and a pH of 1.2 to 3.5 for the tartrate-buffered solution. However, the concentration of the solution of the buffer also has an effect upon the mobility and diffusion of zinc ions. As revealed in Table 4 and Fig. 4, an increase in the sodium citrate concentration leads to a displacement of the deposition potential of zinc, indicating the formation of more stable complex ions of zinc

Fig. 4. Effect of concentration of sodium citrate and tartrate solutions upon the U_{01} and D_1 of zinc ions.

(with citrate ion). The experimental data show that an increase in the concentration of the sodium citrate solutions from 0.01 to 0.60 mole/liter and of the tartrate solution from 0.01 to 0.2 mole/liter diminishes the speed of movement and
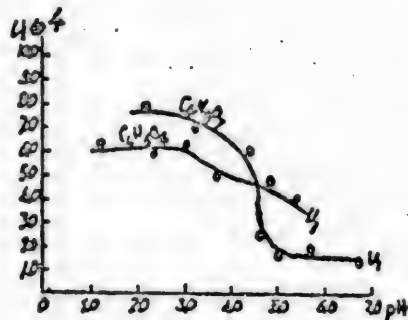
TABLE 4

Influence of the Concentrations and pH of Solutions of Sodium Citrate
and Tartrate upon the U_{oi} and D_i of Zinc Ions

Expt. No.	Concentration		p_H of medium	Height of polarographic wave (in mm)	i_d diffusion current (μA)	u_{oi} (cm/sec. $\cdot 10^{-4}$)	D_i (Cm^2/sec. $\cdot 10^{-6}$)	(E) Deposition potential (in V)
	Sodium citrate (mole/l.)	Sodium tartrate (mole/l.)						
1	0.07	—	2.1	52.0	16.65	7.65	9.70	-1.00
2	0.07	—	3.3	50.0	16.00	7.15	9.00	-1.02
3	0.07	—	4.4	46.0	14.70	6.00	7.60	-1.06
4	0.07	—	4.6	30.0	9.60	2.56	3.24	-1.07
5	0.07	—	5.0	26.0	8.35	1.93	2.46	-1.08
6	0.07	—	5.7	26.0	8.35	1.93	2.46	-1.08
7	0.07	—	6.8	24.0	7.70	1.68	2.10	-1.09
8	0.01	—	3.0	57.0	18.25	7.90	10.1	-0.90
9	0.02	—	3.0	54.0	17.25	7.06	9.10	-0.95
10	0.03	—	3.0	54.0	17.25	7.06	9.10	-0.95
11	0.04	—	3.0	53.0	16.90	6.80	8.80	-0.96
12	0.05	—	3.0	53.0	16.90	6.80	8.80	-0.96
13	0.10	—	3.0	52.0	16.60	6.56	8.45	-0.97
14	0.20	—	3.0	51.0	16.30	6.35	8.20	-0.98
15	0.40	—	3.0	47.0	15.00	5.35	6.90	-0.99
16	0.60	—	3.0	45.0	14.40	4.96	6.40	-1.00
17	—	0.05	1.2	50.0	16.00	6.05	7.90	-1.26
18	—	0.05	2.4	50.0	16.00	6.05	7.90	-1.26
19	—	0.05	3.0	50.0	16.00	6.05	7.90	-1.26
20	—	0.05	3.4	48.0	15.30	5.60	7.20	-1.28
21	—	0.05	3.7	46.0	14.70	5.15	6.65	-1.22
22	—	0.05	4.9	44.0	14.10	4.75	6.12	-1.20
23	—	0.05	5.4	40.0	12.80	3.90	5.05	-1.28
24	—	0.01	3.7	50.0	16.0	6.05	7.90	-1.28
25	—	0.10	3.7	44.0	14.10	4.75	6.12	-1.26
26	—	0.20	3.7	40.0	12.80	3.90	5.05	-1.25

Note to Table 4: 1) Galvanometer sensitivity S - 1/25. 2) Concentration of $ZnSO_4$ solution - $2.10 \cdot 10^{-3}$ mole/l. 3) Capillary constant 2.25 mV x 2/3 sec. $^{-1/2}$. 4) Visual polarograph.

diffusion of zinc ions by roughly 30 per cent.

It also follows from Table 4 (columns 7 and 8) that the speeds of movement and diffusion of zinc ions are generally lower in tartrate-buffered than in citrate-buffered solution (Fig. 4). The phenomenon is clearly due to the formation of more stable complex ions of zinc in the tartrate buffer than in the citrate buffer. This is also confirmed by the more negative reduction potentials during electrolysis of zinc in sodium tartrate solution (Column 9 of Table 4). At a pH of the tartrate-buffered solution higher than 3.0, a decrease in U_{oi} and D_i is observed, although we did not observe a fall in the speed of movement and diffusion as sharp as the fall which occurs in citrate-buffered solution.

SUMMARY

1. The polarographic method is shown to be practicable for the determination of the transference numbers, mobilities, and diffusion coefficients of zinc ions.

2. The limiting current is found to be a rectilinear function of the zinc sulfate concentration.

3. Experiments show that with increasing potassium chloride concentration the U_{01} and D_1 of zinc ions increase. This is evidently due to dehydration of the hydrated zinc ions and to the formation of ions $(ZnCl)$ with a higher mobility than $Zn^{..}$.

4. It was established that the most favorable condition for transference and diffusion of zinc ions to the electrode in tartrate- and citrate-buffered media is an acid medium with a pH of 1.2 to 4.5. A higher pH value markedly retards the transfer of zinc ions to the electrode.

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PRODUCTS OF THERMAL DECOMPOSITION OF CHROMIUM FORMATE

AND THEIR ANALYSIS

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At high temperatures formic acid splits off either carbon dioxide (I) or water (II) or simultaneously water and carbon dioxide (III), two molecules of acid reacting in the latter event.
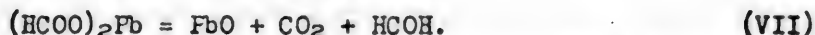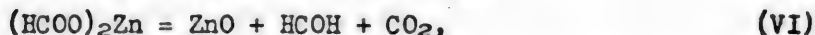
If reactions (I) and (III) proceed simultaneously, then under some conditions hydrogen will react with the formaldehyde and methyl alcohol will be formed, but the yield of the latter is very small.

$$HCOOH = CO_2 + H_2, \qquad \text{(I)}$$

$$HCOOH = CO + H_2O, \qquad \text{(II)}$$

$$2HCOOH = H_2CO + CO_2 + H_2O, \qquad \text{(III)}$$

$$3HCOOH = CH_3OH + 2CO + H_2O. \qquad \text{(IV)}$$

Reaction (I) is a dehydrogenation. It takes place at ordinary temperature with rhodium or palladium black.

The dehydration reaction (II) takes place in presence of dehydrating agents such as H_2SO_4.

The course of decomposition of salts of formic acid varies with the cation. The following reactions [1] are known:

$$(HCOO)_2Ni = Ni + H_2 + 2CO_2, \qquad \text{(I)}$$

$$(HCOO)_2Ni = Ni + H_2O + CO + CO_2, \qquad \text{(II)}$$

$$(HCOO)_2Ca = CaCO_3 + H_2 + CO, \qquad \text{(III)}$$

$$2HCOONa = (COONa)_2 + H_2, \qquad \text{(IV)}$$

$$(HCOO)_2Fe = FeO + H_2 + CO + CO_2, \qquad \text{(V)}$$

$$(HCOO)_2Zn = ZnO + HCOH + CO_2, \qquad \text{(VI)}$$

$$(HCOO)_2Pb = PbO + CO_2 + HCOH. \qquad \text{(VII)}$$

The following mechanism was established by Freidlin and Bulanova [2] on the basis of analysis of the products of decomposition of $(HCOO)_2Pb$:

$$(HCOO)_2Pb \longrightarrow Pb + 2CO_2 + H_2. \qquad \text{(VIII)}$$

Using a vacuum technique, Erofeev made a detailed study of the decomposition of cobalt formate, alone and in admixture with Mn·· formate at 218°. Decomposition proceeds preferentially according to the scheme:

$$(HCOO)_2Co = Co + H_2 + 2CO_2. \qquad \text{(IX)}$$

Hofmann and Schumpelt [1] examined the products of decomposition of nickel formate which had been dried at 90°, and then heated in a current of moist CO_2. Consequently, they only determined the H_2 and CO contents. Their data indicate that the reaction proceeds mainly according to (I) and to a lesser extent according to (II).

They ascribed the lower carbon yield relative to (I) and (II) to the occurrence of reaction (X). They also considered a Boudouard reaction (XI) possible.

$$CO + 3H_2 = CH_4 + H_2O, \qquad \text{(X)}$$

$$2CO = CO_2 + C, \qquad \text{(XI)}$$

$$CO_2 + 4H_2 = CH_4 + 2H_2O. \qquad \text{(XII)}$$

Important contributions in this field were made by Yanysheva and Grigoryan [3], and their studies of the thermal decomposition of nickel formate showed that reactions (I) and (II) at first proceed simultaneously with reaction (I) predominating. After the kinetic curve has reached a minimum, only reaction (I) continues to take place.

Dobychin, Roginsky, and Tselinskaya [4] found that the thermal decomposition of nickel formate proceeds mainly according to reaction (I).

In the present investigation we have prepared and examined the products of decomposition of chromium formate. We did not find any information on this reaction in the literature.

The chromium formate which we prepared was dried at 105-110°.

Anhydrous chromium formate was subjected to thermal decomposition in a current of nitrogen, which made it possible to examine all of the gaseous components entering into the composition of the gas mixture.

In a series of experiments it was established that any appreciable evolution of gases only began at a temperature of about 300°.

The evolved gas mixture comprised CO_2, CO, and H_2, and the residue was CrO_2.

Thermal decomposition of chromium formate is found to proceed according to the reaction:

$$2(HCOO)_3Cr = 2CrO_2 + 2CO_2 + 4CO + 3H_2. \qquad \text{(XIII)}$$

Formation of the intermediate oxide CrO_2, which can be represented as a compound of the two oxides, $CrO_3 \cdot Cr_2O_3$, point to the partial oxidation of Cr^{+3} to Cr^{+6}.

This partial oxidation reaction may be compared with the reaction of carbon dioxide with metallic Mg at the flame temperature of the latter:

$$CO_2 + 2Mg = 2MgO + C. \qquad \text{(XIV)}$$

Formation of metallic chromium at an intermediate stage is highly probable on the analogy of the decomposition of the formates of nickel and cobalt according to equations (I) and (IX).

Such an oxidation may be assumed to proceed according to the equations:

$$2Cr + 3CO_2 = 2CrO_3 + 3C, \qquad \text{(XV)}$$

$$Cr + CO_2 = CrO_2 + C. \qquad \text{(XVI)}$$
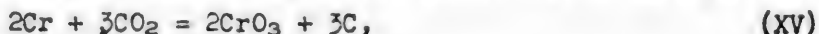
This is rendered even more probable by the fact that the thermal decomposition of chromium formate commences at a fairly high temperature (300° and higher).

The data in the literature and the results of our study lead us to the conclusion that the thermal decomposition of formates can proceed in very diverse directions in dependence on the nature of the cations.

Apart from the principal reaction of formate decomposition, concurrent reactions take place with formation of organic products in addition to formation of carbon according to the Boudouard reaction (X).

EXPERIMENTAL

We prepared chromium fromate from $Cr(NO_3)_3$ which was precipitated with NH_4OH:

$$Cr(NO_3)_3 + 3NH_4OH = Cr(OH)_3 + 3NH_4NO_3. \qquad (XVII)$$
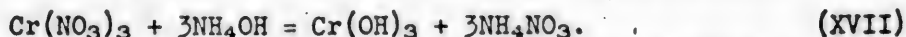
The precipitate of $Cr(OH)_3$ was dissolved in concentrated HCOOH on a water bath at 70-80°:

$$Cr(OH)_3 + 3HCOOH = (HCOO)_3Cr + 3H_2O. \qquad (XVIII)$$

The separated fine green crystals were sucked dry on a Buchner funnel, quickly washed with water and dried in a vacuum desiccator for 24 hours.

The chromium formate was dried at various temperatures. In all of the experiments the water was eliminated from the formate with great difficulty. Experimental results are cited in Table 1.

TABLE 1

Expt. No.	Temperature, °C	Weight before drying, g	Weight after drying, g	Loss of water, g	Loss of water, per cent
During analysis of the formate	105-110	0.222	0.196	0.026	11.3
5	110-120 140-160	0.2924	0.2584	0.034	10.7
9	At expt. temp. of 320°	0.2642	0.236	0.0282	11.7
10	120-130 24 hours	0.552	0.484	0.068	12.3

The composition of the water was not studied. The percentage of Cr in the dehydrated chromium formate was determined.

Decomposition of the formate was carried out in a nitrogen atmosphere in the apparatus described below. The reaction vessel was placed in a bath filled with a fused mixture of KNO_3 (57%) and $NaNO_3$ (43%), this mixture ensuring the temperature conditions required.

A side tube of the reaction vessel, with a tap, was connected to the gasholder, and the open end of the vessel was connected to two gas burets. The entire apparatus was purged several times with nitrogen. The apparatus was tested for tightness after the tap had been closed and the rubber tube which led to the gasholder had been detached. The reaction vessel was then immersed in the bath, which was heated to the experimental temperature of 300° or higher, and then connected to the shaft of a motor (for agitation) before measurements were taken at the burets. At the conclusion of an experiment, the gases in the gas burets were transferred to an Orsat-Lunge apparatus for determination of CO_2, CO, and H_2. The gas remaining in the reaction vessel and in the system was driven into the gas buret by nitrogen and mixed by alternate raising and lowering of the bulb, it was then likewise analyzed in the Orsat-Lunge apparatus.

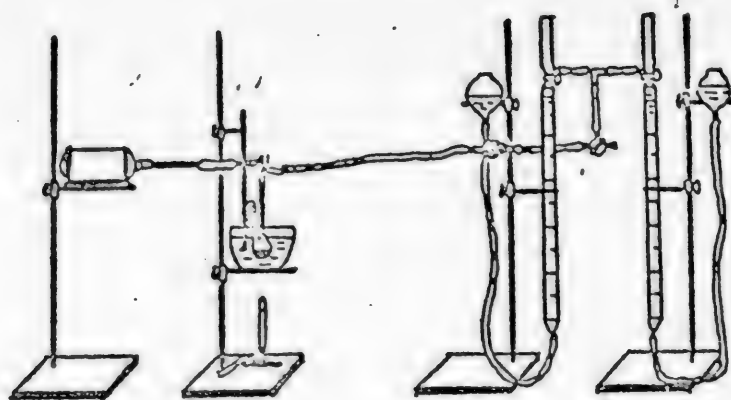The temperature in the gas buret was 20 ± 2°. The gas volumes were not

Fig. 1. Diagram of apparatus.

converted to normal conditions. Readings of the gas volume were taken each minute.

Irregularities were observed in the gas evolution, as shown by Fig. 3. All of the experiments were repeated several times.

RESULTS OF EXPERIMENTS

We studied the kinetics of chromium formate decomposition over the temperature range of 300-340°, (results are collected in Table 2). A series of preliminary experiments showed that appreciable gas evolution occurred at 290-300°.

TABLE 2

Expt. No.	Medium	Temp. °C	Duration of reaction (min)	
3	Nitrogen	340	20	
6,10	Nitrogen	330-340	23,	22
5, 9	Nitrogen	320-330	30,	31
11, 2	Nitrogen	300-320	30,	38

The reaction was arbitrarily considered to have terminated when no appreciable amount of gas was evolved after a period of three minutes (to an accuracy of 0.1 ml). The volumes of gas evolved after time t during the decomposition of the formate in nitrogen are shown in Fig. 2.

Figs. 2 and 3 show that at the low temperature of 300-310°, the velocity is practically constant, but a maximum is formed at a higher temperature and rises further with extraordinary rapidity with further temperature rise (Fig. 3).

Fig. 2. Volumes, V, of gas evolved after time t during decomposition of chromium formate in nitrogen.

A-300 310°, wt. 0.229 g., expt. 11; B 330-340°, wt. 0.24 g., expt. 10; C · 340°, wt. 0 346 g., expt. 3.

We found that the thermal decomposition of chromium formate proceeds mainly according to reaction (XIII). This was established by analyses of the evolved gases at various parts of the curve: at the start of an experiment, in the middle, and at
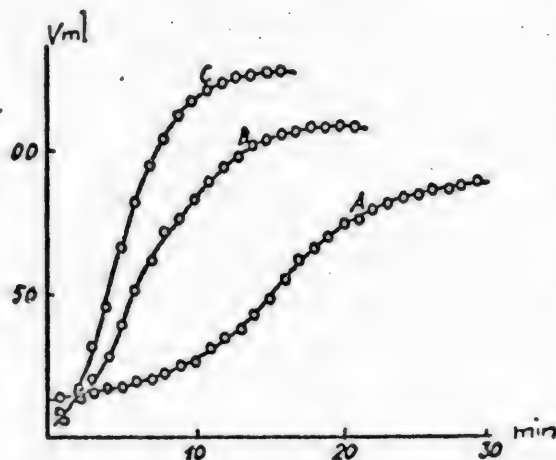
the end. Analyses in all these cases revealed an identical ratio without any noteworthy deviation (Table 3).

About 4 moles of gases were found as compared with the 4.5 moles required by reaction (XIII). The ratio of CO to CO_2 was roughly 1, whereas reaction (XIII) requires a ratio of 2.

In a study of the products of decomposition of anhydrous nickel formate, Hofmann and Schumpelt observed a deficiency of carbon in relation to what was required by reactions (I) and (II), and they proposed reaction (X) to account for this. They also considered the Boudouard reactions to be possible:

$$CO + 3H_2 = CH_4 + H_2O,$$

$$2CO = CO_2 + C.$$
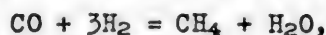
Yanysheva and Grigoryan, working with dehydrated nickel formate, found less carbon in the gas composition than expected, and also an excessive amount of solid residue, calculated on the basis of metallic nickel.

We observed an analogous picture in the thermal decomposition of chromium formate.

Throughout the duration of each experiment the CO amount was less than anticipated from reaction (XIII), and in all cases the amount of solid residue, calculated as CrO_2, was too high. We determined the Cr content of the latter. It was soluble with difficulty in acids, but it readily oxidized when fused with a mixture of KNO_3 and sodium carbonate in a platinum crucible. The percentage of Cr was determined gravimetrically [5]. The Cr content of the CrO_2 is shown in Table 4.
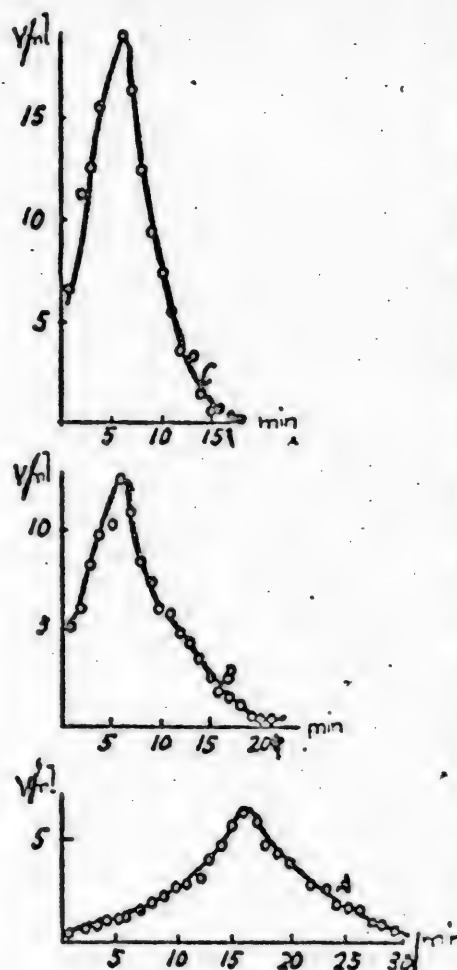

Fig. 3. Effect of the velocity of formate decomposition upon the form of the kinetic curves.

TABLE 3

Expt. No.	Weight of formate, g	Gases (in ml)						Total amount of gases (ml)	
		CO_2		CO		H_2			
		Computed	Found	Computed	Found	Computed	Found	Computed	Found
9	0.236	28.1	37.0	56.2	35.8	42.2	39.4	126.5	112.2
10	0.240	28.8	37.2	57.6	36.0	43.2	41.4	129.7	114.4

An experiment was designed to show that carbon was present in the solid residue even though the latter could still be represented by the formula CrO_2.

A weighed quantity of the solid residue obtained after thermal decomposition of the formate was placed in a porcelain boat in a quartz tube which was connected at one end to a gasholder and at the other end to the measuring buret of an Orsat-Lunge apparatus. Nitrogen was introduced into the system through

copper heated to 600°.

In the atmosphere of nitrogen the solid residue was observed to undergo spontaneous combustion and a change of volume took place in the measuring buret.

When the spontaneous combustion had come to an end, heating was continued for another hour before the gas was analyzed. It was found to be carbon monoxide (Table 5).

TABLE 4
Determinations of Cr in CrO_2

Expt. No.	Wt. of CrO_2, g	$BaCrO_4$, g	Percent Cr	
			Found	Computed
1	0.0706	0.2142	62.1	61.9
2	0.0466	0.1440	62.9	

TABLE 5

Expt. No.	CrO_2, g	Cr_2O_3 (in g)		CO			O_2 (g)		O_2 not lost by combustion, g	C, (g) present in the CO
		Computed	Found	Loss in weight	(Ml)	g	Computed	Found		
9	0.114	0.096	0.0962	0.0178	12	0.015	0.0108	0.0084	0.0024	0.0066
10	0.118	0.098	0.0988	0.0192	14.6	0.0182	0.0112	0.0104	0.0008	0.0078

The spontaneous combustion in nitrogen could only be explained by the fact that at a temperature of 600°, the solid residue — the oxide CrO_2 — lost oxygen with formation of Cr_2O_3:

$$2CrO_2 = Cr_2O_3 + O. \qquad (XIX)$$

The carbon present, which caused the weight of solid residue, as given in Table 4, to be too high, coupled with a too-small amount of oxygen for complete combustion of the carbon to CO_2, led to the formation of CO.

The ability of chromic anhydride, CrO_3, to lose part of its oxygen at a high temperature and to be converted into the lower oxides CrO_2 and Cr_2O_3 has been established by a number of investigations [6].

To obtain still further confirmation of the previous results, the solid residue obtained after heating in the quartz tube at 600°, assumed to be Cr_2O_3, was analyzed for its Cr content, [6].

TABLE 6

Expt. No.	Wt. of Cr_2O_3 g	$BaCrO_4$, g	Percent Cr	
			Found	Computed
1	0.0424	0.1464	70.8	68.6
2	0.0524	0.1780	69.9	—

Results of analysis of the solid residue for the percentage of Cr in Cr_2O_3 after ignition at 600° are given in Table 6.

A complete analysis of the solid residue which we performed allowed us to ascribe to it the formula CrO_3.

SUMMARY

1. We prepared chromium formate. It crystallizes in the form of regular, very fine green needles.

2. Both a preliminary analysis and an analysis of the products of thermal decomposition indicated that the chemical formula was $Cr(HCOO)_3$.

3. Analyses were made of the gaseous and solid products of thermal decomposition of chromium formate. Decomposition proceeds primarily according to the

equation:

$$2Cr(HCOO)_3 = 2CrO_2 + 2CO_2 + 4CO + 3H_2.$$
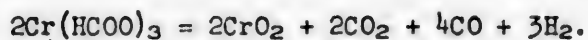
4. The thermal decomposition of chromium formate is a complex reaction, as evidenced by the formation of the intermediate oxide CrO_2 and by the presence of carbon in the solid residue. Formation of the main bulk of the carbon may be ascribed to the Boudouard reaction. Partial oxidation of Cr^{+3} is possible by interaction of metallic Cr with carbon dioxide.

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MODIFICATION OF COMPLETE OXIDATION CATALYSTS

L. Ya. Margolis and O. M. Todes

The effect of additives upon the catalytic activity of solids has been the subject of study by numerous investigators [1]. Interesting results were obtained in an examination of the effect of additives upon the catalytic properties of metallic films [1]. Small amounts of impurities which are retained in the process of preparation of the catalyst are capable of increasing the activity many times (promotion) [3], whereas large proportions markedly diminish the activity (poisoning).

Starting from these facts, S.Z. Roginsky developed the concept of the dual character of the influence of additives upon catalytic activity. It had been generally considered that there was no relation between the two phenomena of poisoning and promotion and that they differed qualitatively in their mechanisms. In particular it had been assumed that the poisoning of a catalyst always involves a simple blocking of a portion of the active surface by the inactive admixture.

S.Z. Roginsky, however, on the basis of experimental studies on micropromotion with gases, developed the theory that underlying the phenomena of poisoning and promotion in a series of cases is a common mechanism involving a change in the kinetic constants of the catalyst. In particular, to account for the observed changes during micropromotion he postulated that the admixtures change the activation energy of the catalytic process in the sense that very small amounts of them reduce the energy and promote the catalyst, while large amounts increase the energy to produce the effect of poisoning.

Working in the same laboratory, we ourselves have made a careful kinetic study over a period of years of the catalytic reactions of complete oxidation of hydrocarbons over a group of catalysts possessing a spinel structure. These catalysts are compounds of the type of Me''Me$_2$O$_4$ with admixture of the free oxide Me''O. Such compounds have a great tendency to retain admixtures with formation of solid solutions.

During the complete oxidation of hydrocarbons over these catalysts we made a close investigation of the characteristics of the process and established the following facts:

1. The more active a catalyst is under given conditions, the greater the activation energy of the oxidation reaction.

2. Changing energy of activation is accompanied by a marked change in the exponent entering into the expression for the constant of the reaction velocity.

We deemed it interesting, in connection with the foregoing observations, to make an exhaustive study of the effect of small amounts of additives on this

class of catalysts. Since the kinetics of the catalytic reaction over the original catalysts had already been investigated, it was possible to make a direct study of the effect of additives upon the chief kinetic constants – the activation energy and the exponential factor. Our investigation, the detailed results of which are presented in this paper, revealed a very pronounced and consistent effect of small amounts of additives upon both of these kinetic characteristics and made it possible to introduce corrections and improvements into Roginsky's hypothesis of the mechanism of the dual effect of additives.

Examination of the preliminary data of our work, as well as of certain other studies in the laboratory, indicated the existence of a widespread group of phenomena involving "modification" of catalysts. The implications of this new concept are discussed in more detail in a series of papers and communications by S.Z.Roginsky.

EXPERIMENTAL

1. a) Catalysts. As representatives of the above-mentioned spinel catalysts we selected the magnesium-chromium complex $MgCr_2O_4$ + MgO and the copper-chromium complex $CuCr_2O_4$ + CuO. These catalysts differ considerably from each other in activity and in the values of the activation energies and exponential factors during the combustion of isooctane in their presence [4]:

	Activation Energy, E	Logarithm of the exponential factor, $\log K_0$
Magnesium-chromium Mg – Cr..	45,000	17.0
Copper-chromium Cu – Cr	15,500	6.0

b) Additives. We selected oxidation-resistant and difficultly volatile inorganic acids and their salts as the components influencing the catalytic ac-activity: 1) orthophosphoric acid, H_3PO_4; 2) boric acid, H_3BO_4; 3) barium sulfate $BaSO_4$; 4) sodium silicate, Na_2SiO_3; 5) barium nitrate, $Ba(NO_3)_2$; and 6) hydrofluoric acid, HF.

c) Preparation of catalysts. The original catalyst in powder form was treated with a solution of the additive of known concentration which was so sele-selected that the whole of the solution was absorbed by the powder. In the case of compounds insoluble in water, such as $BaSO_4$, the catalyst was successively treated with solutions containing the barium ion (e.g. $BaCl_2$) and SO_4'' (e.g. Na_2SO_4), and then washed to remove $NaCl$. After the treatment, the catalyst was allowed to stand for 12-16 hours before being deposited upon an asbestos support from an aqueous suspension. It was finally dried at 100°. Concentrations of additives varied from 0.5 to 10% by weight of the initial catalyst. In separate experiments it was established that none of these additives, deposited on a support in proportions up to 20% by weight, catalyzed the oxidation of isooctane under our conditions. All of the systems of catalysts were studied in relation to the complete oxidation of isooctane.

d) Specific surface and structure. Measurements of the molecular adsorption of nitrogen at a temperature of -190° and of the specific surface of these catalysts were performed on one of the series of catalysts (magnesium-chromium with addition of phosphoric acid). As shown in Table 1, the specific surface of these catalysts is substantially constant. Similar data were obtained by S. Yu.Elovich in the adsorption of propene (at -63°) on these catalysts.

X-ray examination of the pure catalysts showed that the magnesium-chromium and copper-chromium catalysts are actually spinels containing an excess of free metallic oxide.

2. Effect of the Modifying Additives Upon the Velocity of Oxidation of Isooctane

The yield of the final product of oxidation of isooctane (carbon dioxide) varied with incorporation of different additives in the catalysts (Mg–Cr and Cu–Cr).

TABLE 1

Specific Surface of Magnesium-Chromium Catalyst with Addition of Phosphoric Acid

Catalyst	Additive, %	Surface (in m^2/g).
Mg – Cr	1.0	61.0
	1.5	68.0
	2.0	69.0
	3.0	62.0

Figure 1 contains a plot of the CO_2 yield as a function of the phosphoric acid content of magnesium-chromium and copper-chromium catalysts. The curves exhibit both a maximum and a minimum which at first glance is inexplicable. Later, however, we shall show that the discontinuities are a regular occurrence. It is shown in Fig. 2 that with the
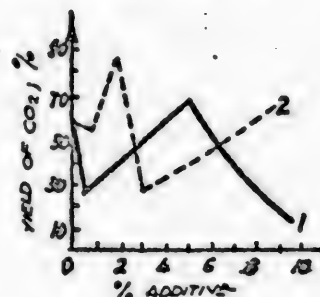

Fig. 1. Dependence of the carbon dioxide yield upon the content of phosphoric acid in magnesium-chromium and copper-chromium catalyst (at T = 350°, isooctane concentration in the air C_0 = 1.77%)

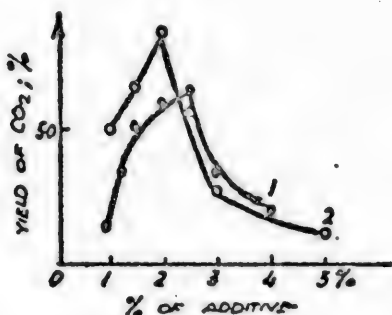1-Magnesium-chromium + H_3PO_4 .

2-Copper-chromium + H_3PO_4

Fig. 2. Dependence of the CO_2 yield upon the content of phosphoric acid and sodium silicate in magnesium-chromium catalyst at T = 300°, (concentration of isooctane in air C_0 = 1.77%).

1-Magnesium-chromium + H_3PO_4 . 2-magnesium-chromium + + H_3PO_4

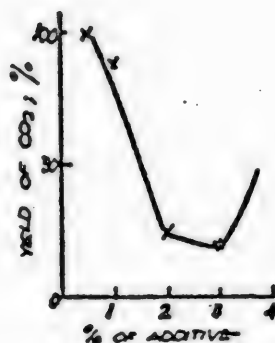

Fig. 3. Dependence of CO_2 yield upon the barium nitrate content of the magnesium-chromium catalyst (at T = 150°, C_0 = 1.77%).

introduction of sodium silicate and phosphoric acid into magnesium chromite, the CO_2 yield reaches a maximum at a certain concentration of additive and then falls again. In other words, the catalytic activity at a given temperature at first rises and then falls. Using barium nitrate in this catalyst, it was possible to reduce the reaction temperature by nearly 200°, and here it was found that the CO_2 yield falls up to a certain limit (nearly 5 times) at a certain additive

content and then again increases (Fig. 3). Although these plots alone indicate the broad effect of small concentrations of additives upon the activity of the catalyst, it is impossible to regard the CO_2 yield as a principal criterion, since in dependence upon the thermal conditions, upon the initial hydrocarbon concentration, and upon the kinetic law, the yield is not a comparable magnitude and will give an erroneous impression.

3. Effect of Modifying Additives upon the Kinetic Oxidation Law

Activity of the catalyst. For all of the catalyst systems a close study was made of the kinetics of oxidation of isooctane, and the velocity constants were calculated.

With progressive increase in the additive content of the catalyst, the reaction order steadily decreased from second (for pure catalysts the oxidation of isooctane obeys the square root law) to first, and for a series of additives when present in high concentration it falls to zero. In the region of additive concentration in which the reaction is first order, the plots of CO_2 yield versus concentration have a regular course without unexpected discontinuities (Fig. 2). Within these limits the velocity constant increases exponentially with the temperature in accordance with the Arrhenius law in the region of 150°.

In earlier papers [4] we had already noted the intersections of the plots of log K versus 1/T which are characteristic of this process and this system of catalysts, and which indicated that a catalyst possessing maximum activity in one temperature region became least active in another region. We likewise observed an intersection of the log K – 1/T plots for catalysts with various additives in various concentrations.

The relation: $\log K = \underline{f}(1/T)$ is plotted in Fig. 4 for various concentrations of additive.

If two temperature sections are taken in this diagram (the straight lines $\underline{a}$ and b), then at the low temperature the pure catalyst

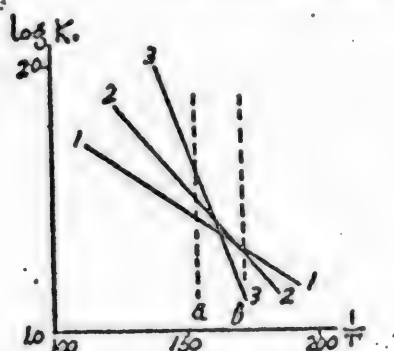

Fig. 4. Schematic representation of the dependence of log K on $\underline{f}(1/T)$ for various concentrations of an additive.
1-pure, G = 0; 2 - G=G₂; 3 - G=G₃ < G₂; a,b - limits of temperature zone of intersection.

Fig. 5. Dependence of the velocity constant of the reaction upon the proportion of sodium silicate admixed with magnesium-chromium catalyst.
1- at T = 300° (square root law) $[K_{sq}]$;
2- at T = 400° (first order) $[K_1]$.

is the most active and all of the catalysts containing additive are less active, and in this case the additive must function as a poison. Curve A_G, percent of additive G, must first fall and then rise to its original position. Conversely, at high temperatures, the pure catalyst is the most inactive, and curve
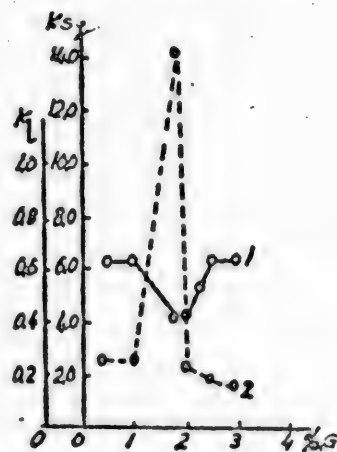
A_G, per cent of additive G, must have a maximum at values which formerly resulted in a minimum..

We observed this characteristic effect of additives in all of the systems investigated. The activity of a catalyst is expressed in the form of values of the velocity constant, which enabled a comparison of a catalyst within the limits of a single reaction law. In Figs. 5, 6, and 7 are represented the variations in velocity constants with the percentage of additive in the catalyst. In one temperature region a prominent maximum is observed, i.e., increasing activity of the catalyst, while in another region a characteristic minimum appears, i.e., a fall in catalytic activity at a given additive concentration. Maximum and minimum activity correspond to one and the same additive concentration.
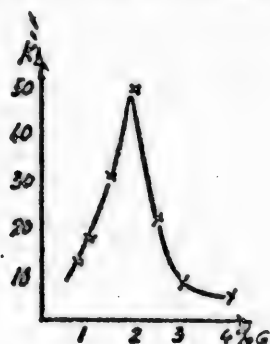

Fig. 6. Dependence of the velocity constant upon the phosphoric acid content of magnesium-chromium catalyst (at T = 350°).
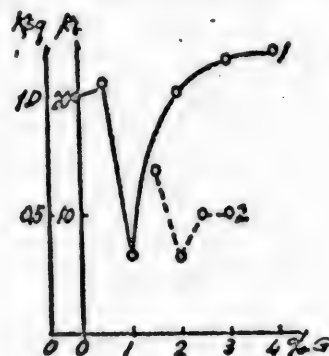

Fig. 7. Dependence of the velocity constant upon the phosphoric acid content of Mg — Cr and Cu — Cr catalysts.

1-Copper-chromium, T=300° (square root law) $[K_\sqrt{}]$
2 Magnesium-chromium, T=300° (first order) K_1

4. Effect of Modifying Additives upon the Values of Activation Energy and Exponential Factors

With introduction of additives into a catalyst, within the limits of a given reaction order the activation energies and exponential factors change considerably in proportion to the additive content (Tables 2-5 and Figs. 8-12).

With increasing concentration of additive in all the investigated systems, the values of E and K_0 rise at first, simultaneously reaching their maxima, and then begin to fall in unison. It should be noted that this change in the values of E and K_0 reaches a very considerable magnitude. Thus, the activation energy changes from 5,000 cal/mole to 30,000 cal/mole, while K_0 alters by a factor of 10^{10}.

A linear relation exists between the activation energy and the logarithm of the exponential factor for catalysts with different additives (Fig. 13). For each additive, with increasing concentration, the points plotted in Fig. 13 at first move along a straight line to the right and upwards, reach values of E and log K_0 which are maxima for a given additive, and then begin to move to the left and downwards along the same straight line. This is a fresh example of the previously noted dependence [6], the nature of which has not hitherto been adequately

TABLE 2

Effect of Admixture of Phosphoric Acid with
Magnesium Chromite
Catalyst: Mg-Cr.   Additive: H_3PO_4

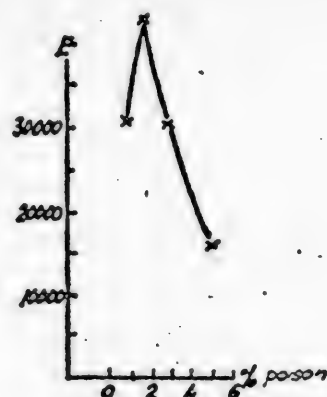| % additive	Reaction order	Activation energy (E)	Logarithm of the exponential factor (log K_0)	Temperature
0	2	40000	14	250-500°
1	2	38000	15	280-325
1	1	7200	3.8	325-500
1.5	1	10300	5.0	300-450
2.0	1	40000	16.0	300-400
2.5	1	11200	5.0	300-400
3.0	1	9500	4.5	300-500
5.0	1	7200	3.5	325-500
7.0	1	6600	3.2	325-500
8.0	0	23000	10	325-400

Fig. 8. Dependence of the activation energy upon the barium sulfate content of magnesium-chromium catalyst.

TABLE 3

Effect of Admixture of Phosphoric Acid with
Copper Chromite
Catalyst: Cu-Cr;   Additive: H_3PO_4

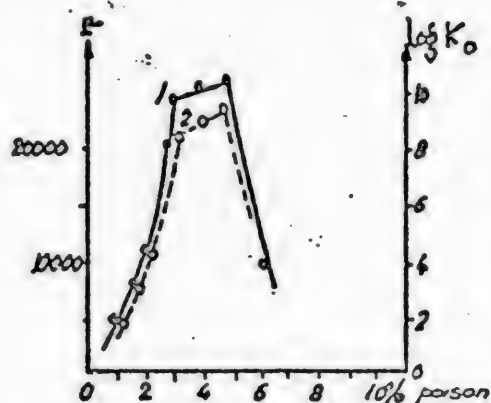| % Additive	Reaction order	Activation energy (E)	Logarithm of the exponential factor (log K_0)	Temperature
0.5	2	13000	4.5	300-500°
1.0	2	13000	4.5	300-450
2.0	2	13300	4.7	300-400
2.0	1	11000	4.0	400-500
3.0	2	10000	4.0	300-400
3.0	1	24000	8.5	430-470
4.0	1	24000	8.7	325-450
5.0	1	26000	8.8	400-450
6.0	0	9700	5.5	300-425
7.0	0	8600	4.7	300-500
10.0	0	9000	4.7	300-500

Fig. 9. Dependence of the activation energy and logarithm of the exponential factor upon the phosphoric acid content of Cu-Cr catalyst.

1-Activation energy E. 2 logarithm of the exponential factor log K_0.

understood.

Addition of hydrofluoric acid to chromites, like the addition of other components, changes the order of the reaction, but in this case the changes in energies of activation and exponential factor with increasing concentration are small (log K_0 changes by less than 1), and thus the main feature of the changes effected by this additive cannot be studied.

TABLE 4

Effect of Admixture of Sodium Silicate
with Mg-Cr and Cu-Cr catalysts

Additive, %	Reaction order	Activation energy E	Logarithm of the exponential factor (log K_O)
Cu-Cr catalyst			
0.5		8600	3.0
1.0		8600	3.0
1.5		9200	3.2
1.8	1st	24500	9.3
2.0		19200	6.4
2.3		9000	3.2
2.5		9000	3.2
3.0		8000	2.8
Mg-Cr catalyst			
1.5		7200	3.9
1.8		37000	15.7
2.0	1st	38000	16.5
2.5		26800	11.8
3.0		10900	6.5
4.0		10900	6.5

TABLE 5

Effect of addition of Barium Nitrate to
Magnesium Chromite: Catalyst Mg-Cr;
Additive $Ba(NO_3)_2$

Additive, %	Reaction order	Activation Energy, E	Logarithm of the exponential factor, (log K_O)
0.5		20500	12.4
1.0		21800	12.5
2.0	1st	24600	13.4
3.0		32000	.17.4
4.0		18600	11.2
5.0		13000	3.0

5. Effects of Additives on Vanadium Pentoxide

The effect of small amounts of admixtures of strong acids and their salts on binary oxide catalysts has been clearly demonstrated. We thought it necessary to establish whether the characteristic effect also extended to the pure oxides of metals. For this purpose we selected vanadium pentoxide, which is a strong oxidation catalyst widely used in industry for the oxidation of SO_2, toluene, etc.
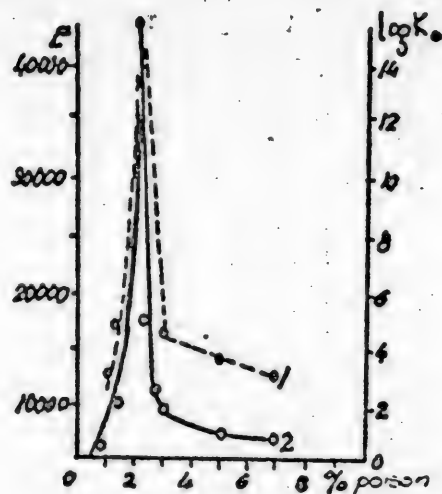

Fig. 10. Dependence of the activation energy and log K_O on the phosphoric acid content of Mg-Cr catalyst.

1-Activation energy,E; 2-logarithm of the exponential factor log K_O.
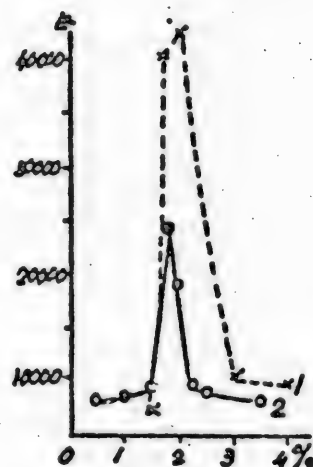

Fig. 11. Dependence of activation energy on content of sodium silicate in Mg-Cr and Cu-Cr catalysts.
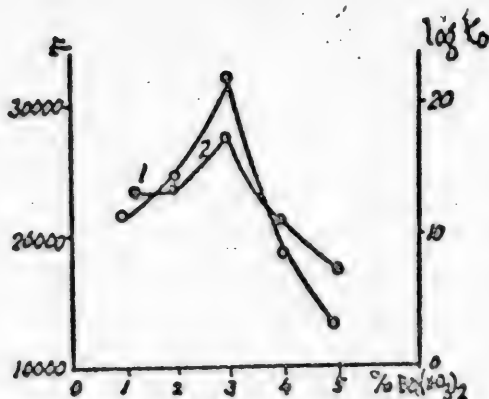
1: Mg-Cr; 2: Cu-Cr.

Fig. 12. Dependence of E and log K_0 on the barium nitrate content of Mg-Cr catalyst.

1-Activation energy, E; 2-logarithm of the exponential factor k_0.

Fig. 13. Dependence of the logarithm of the exponential factor upon the activation energy during the action of various additives on Mg-Cr and Cu-Cr catalysts.

0 Mg-Cr: 1-1.0%, 2-1.5%, 3-2.0%, 4-2.5% H_3PO_4 ;
0 Mg-Cr: 1-1%, 2-2%, 3-3%, 4-5% $BaSO_4$;
X Cu-Cr: 1-2%, 2-3%, 3-4%, 4-6% H_3PO_4 ;
0 Cu-Cr: I-0.5%, II-1.0%, III-2.0% H_3BO_4.

The starting material was analytically pure V_2O_5. The action of phosphoric acid upon V_2O_5 was not accompanied by the features of the phenomenon described above. Vanadium pentoxide is a typical oxide with clearly marked acidic properties. The additive selected was therefore KOH. Fig. 14 shows the change in CO_2 yield as a function of the KOH content of the vanadium pentoxide. On the same graph the effect of KOH on magnesium chromite is plotted for comparison. With change of concentration of KOH up to 3%, the

TABLE 6

Effect of Addition of KOH to V_2O_5
Catalyst: V_2O_5; Additive: KOH

Additive, %	Reaction order	Activation energy, E	Logarithm of the exponential factor, log K_0
0		5400	2.0
1.0		6700	2.8
1.8		7400	3.4
2.0		7600	3.4
3.0		8800	4.8
4.0	1st	16000	6.4
5.0		9200	3.2
7.0		9500	3.2
10.0		5700	2.1

Fig. 14. Dependence of the CO_2 yield on the KOH content of Mg-Cr catalyst and vanadium pentoxide.

1: Mg-Cr. 2: V_2O_5.

CO_2 yield for Mg-Cr + KOH does not vary, whereas for the system V_2O_5 + KOH, the CO_2 yield at first rises and then falls.

In Table 6 and Figure 15 are presented the characteristic changes of activation energy and exponential factor in dependence on the KOH content of V_2O_5. It can be seen that the phenomena of

modification also occur in a pure metallic
oxide.

Evaluation of Results and Summary

The effects of small proportions of
additives on various systems of oxidation
catalysts are the following:

1. The order of the reaction is gen-
erally reduced.

2. Within the limits of a single re-
action order the activation energy and the
exponential factor change concurrently.

3. The maxima are reached simultan-
eously on the plots of additive concentra-
tion versus activation energy and exponen-
tial factor.

4. A linear relation exists between
the activation energy and the logarithm
of the exponential factor.

Fig. 15. Activation energy E and
logarithm of the exponential fac-
tor K_O as functions of the amount
of KOH added to vanadium pentoxide.

1-activation energy, E: 2-logarithm of the
exponential factor K_o.

5. The concurrent change of E and K_O
automatically leads at different tempera-
tures to reversal of the activity relationships of the catalysts.

6. There is no simple relation between the activity (A) and the additive
concentration (G), such as is naturally derived in the conventional treatment of
the effect of additives both for homogeneous and heterogeneous surfaces.

7. One and the same amount of additive may function both as a promoter and
a poison in different temperature regions.

8. The results led to a certain amount of revision and tightening-up of the
concepts previously adumbrated by S.Z.Roginsky on the mechanism of the dual ac-
tion of additives on the activity of catalysts. It was shown that a whole series
of additives affect not only the activation energy of a reaction but also cause
a simultaneous change in the magnitude of the exponential factor, resulting in
turn in a whole series of characteristic changes in the intensity of catalytic
activity. This group of phenomena is outside the framework of the usual termin-
ology of poisoning and promotion of catalysts, and has been classed by S.Z.
Roginsky under the heading of "modification".

9. Modification cannot be explained by the blocking of the homogeneous or
heterogeneous surface, since the blocking of a proportion of the active zones
under a given set of conditions must lead to diminution in the over-all activity
of the catalyst.

Nor can these phenomena be explained by the assumption of development of
specific chemical compounds from the additive and the catalyst, inasmuch as the
modifying additives alter the kinetic performance of the catalyst in a highly
characteristic way.

10. Strong inorganic acids serve as modifying additives for chromite cat-
alysts containing an excess of a basic oxide.

Conversely, effective modifying agents for vanadium pentoxide, which has
highly pronounced acid properties, are caustic alkalies.

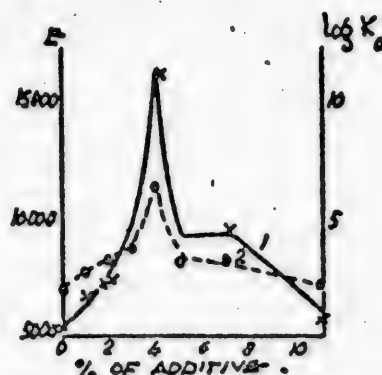11. Modification will naturally be expected not to result in any simple

change of the absolute value of the activity, nor in any profound change in the character of the surface which would lead to more complex changes at the individual stages of a reaction.

12. The inadequacy is demonstrated of existing conceptions about catalysts and about the agents reducing the activation energy of a reaction.

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MODIFICATION OF CATALYSTS. II.

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The term "modification" in relation to catalysts refers to the dual and un-usual changes in activity in presence of additives; such changes cannot without reservation be regarded as either poisoning or promotion. Modifying additives behave in some cases like catalyst poisons, and in others like promoters [1]. With the aim of establishing the extent to which this phenomenon is general, we have undertaken further studies of the modification of catalysts.

In this paper we present studies on other catalysts and other catalytic reactions. More specifically we deal with the kinetics of oxidation of ethylene over magnesium-chromium catalysts ($MgCr_2O_4$ + MgO) modified by admixture of sodium silicate (Na_2SiO_3) and used by Margolis and Todes for the oxidation of isooctane [2].

The kinetics of oxidation were studied in a flow system, using the apparatus described by Margolis and Todes [3], but modified by substitution of a gasholder containing ethylene for the vessel containing liquid isooctane in front of the flowmeter. The speed of admission of ethylene and air was regulated by flow-meters, and the two streams were then mixed in a mixing vessel before entering the reaction vessel. The reaction vessel, the system of traps after the reaction vessel for condensation of the water of reaction, and the electric gas analyzer providing for continuous reading of the CO_2 content were identical with the equipment previously described [3]; a minor change was the use of solid carbon dioxide (-78°) in place of solid chloroform (-62°) in the last trap.

The prepared magnesium-chromium catalyst was treated with a specified quan-tity of silicic acid (in the form of a solution of Na_2SiO_3). The suspension was then placed on asbestos wool and the whole was dried at 100°. The additive content ranged from 1.5 to 5 weight per cent of the original catalyst. The con-centration of catalyst on the asbestos was 1-3% by weight. The amount of asbes-tos for each portion of catalyst charged into the reaction vessel was 3 g in all cases. Preliminary experiments revealed the previously noted proportionality between activity (i.e., the velocity constant of ethylene oxidation) and concen-tration of catalyst on the asbestos. Consequently we were able to use the spec-ific velocity constant to characterize the activity:

$$K_{spec.} = \frac{K}{\text{concn. of catalyst}} \tag{1}$$

For determination of the kinetic equation of ethylene oxidation $C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$, we varied the initial concentration of ethylene from approximately the stoichiometric proportion to half this amount. The space velocity of the stream was 20 liters/hour in all cases. The percentage of oxidized ethylene was found to be substantially independent of the ethylene concentration of the stream,

TABLE 1

Velocity Constants, Activation Energy and Exponential Factor Using Magnesium-Chromium Catalyst Modified with Sodium Silicate

Catalyst concentration, %	Na_2SiO_3 content, wt. %	Temperature °C	Mean value of velocity constant, K_1	Specific velocity constant, $K_{spec.}$	log K_0	Activation energy E, (cal/mole)
2.0	1.5	280	0.063	0.031	3.8	13300
		300	0.093	0.047		
		320	0.145	0.073		
		340	0.21	0.105		
		360	0.32	0.16		
		440	1.32	0.66		
2.0	2.0	250	0.092	0.046	4.9	15500
		260	0.12	0.06		
		300	0.26	0.13		
		310	0.31	0.15		
		320	0.35	0.18		
		340	0.46	0.23		
		360	0.78	0.39		
		390	1.67	0.83		
1.0	2.5	320	0.12	0.12	3.30	11500
		340	0.23	0.23		
		370	0.25	0.25		
		380	0.34	0.34		
		400	0.41	0.41		
		420	0.51	0.51		
		430	0.55	0.55		
		440	0.62	0.62		
		460	0.75	0.75		
		470	0.83	0.83		
2.0	4.0	260	0.060	0.030	1.8	8400
		280	0.052	0.026		
		290	0.062	0.031		
		300	0.075	0.038		
		320	0.092	0.046		
		340	0.14	0.070		
		400	0.16	0.080		
2.0	5.0	320	0.20	0.100	1.7	7300
		360	0.26	0.13		
		380	0.31	0.16		
		400	0.40	0.20		
		410	0.46	0.23		
		420	0.57	0.28		
		460	0.59	0.30		
		470	0.64	0.32		
		510	0.75	0.38		
		520	0.83	0.41		
		560	0.87	0.44		

which indicatesa first order reaction. Results of calculations of the velocity
constant of ethylene oxidation over magnesium-chromium catalyst with admixture
of Na_2SiO_3 are shown in Table 1. Calculations were based on the equation:

$$K_1 = \frac{2.3}{b_0\tau} \log \frac{1}{1-y},\qquad (2)$$

where $b_0 = 20.5$, the oxygen concentration (in volume per cent), $\tau = 0.051$, the
duration of contact in minutes, y = percentage of carbon dioxide in the mixture
after the reaction vessel. The temperature range investigated was 260-470° C.
Further rise of temperature caused spontaneous combustion and the reaction moved
into the diffusion region.

The same table contains values
of activation energy E and the
logarithm of the exponential fac-
tor K_O, calculated from the Arr-
henius equation.

In Fig. 1 is plotted the de-
pendence of log K_{spec}. on $f(1/T)$.
The experimental values of the spec-
ific velocity constant lie on Arr-
henius straight lines.

The rectilinear character of
the relation between the logarithm
of the exponential factor and the
velocity constant of ethylene oxid-
ation is much less pronounced than
in the corresponding study on iso-
octane by Margolis and Todes [1],
using acid treated catalysts. How-
ever, as is clear from Fig. 2, in
our case the correspondence between
the changes of log K_O and E is gen-
erally maintained for the various
catalysts. The exponential factor

Fig. 1. Dependence of the logarithm of
the velocity constant on the reciprocal
of the temperature during oxidation of
ethylene over magnesium-chromium cat-
alyst containing various proportions
of Na_2SiO_3.
1-1.5%; 2-2.0 ; 3-2.5%; 4-4.0%; 5-5.0%.

and activation energy reach a maximum at 2% content of Na_2SiO_3, in the magnesium-
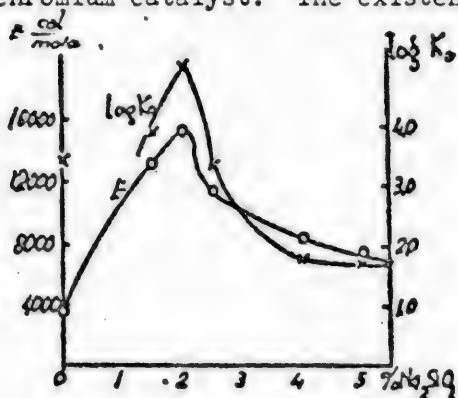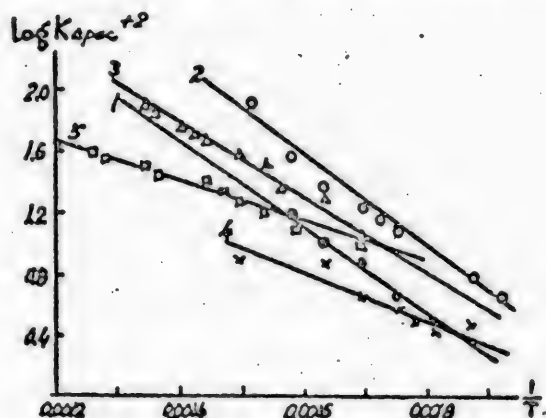chromium catalyst. The existence of a modifying action was also confirmed in
this case.

The second part of this paper is de-
voted to a study of other catalysts with
reference to the phenomenon of modifica-
tion. We investigated the oxidation of
isooctane over tungstic oxide admixed
with caustic alkali.

In their study of the relative behav-
ior of catalysts for the complete oxida-
tion of organic compounds, Elovich, Zhab-
rova, Margolis and Roginsky [4] found that
only oxides of the transition elements of
the periodic system manifest catalytic
activity in such reactions. Of these ox-
ides, those that are non-colored (white)
or weakly colored, such as the oxides of
lanthanum, niobium, yttrium and molybdenum,

Fig. 2. Dependence of the activa-
tion energy and the logarithm of
the exponential factor on the ad-
ditive content of Mg-Cr catalyst.

do not possess appreciable catalytic activity.

In this connection, it was of interest to examine the catalytic effect of tungstic oxide WO_3 in oxidation reactions. Tungsten belongs to the sixth subgroup of the periodic system and is thus a transition element; it forms a series of colored oxides of various valencies which in their turn are capable of forming mixed oxides of varying composition [5].

Tungstic oxide has received relatively little attention as a catalyst for organic oxidations and the properties reported in the literature point to an arbitrary behavior. In the monograph of Marek and Gan [6], some information is given from patents on the utilization of tungstic oxide for the catalytic oxidation of hydrocarbons. Charlot [7] studied the oxidation of toluene, diphenylmethane, naphthalene, ethylbenzene, n-pentane, ethyl and benzyl alcohols, benzoic acid, xylene, o-cresol, and o-toluidine over the following oxide catalysts: oxides of magnesium, tin, cobalt, chromium, vanadium, nickel, tungsten and molybdenum in the temperature range of 250-450°. According to his data the majority of the catalysts give rise to products of both partial oxidation and complete (CO_2 + H_2O) oxidation. Tungstic oxide, WO_3, according to Charlot is much more active than MgO and MoO_3, but less active than NiO, and it gives appreciable amounts of CO_2 at 350-400°. Unfortunately, Charlot's data do not enable the calculation of the velocity constants and activation energies since he only gives the volumes of CO_2 formed after a specified period of time.

We made use of chemically pure tungstic acid in preparing tungstic oxide. Analysis of the acid gave 100% H_2WO_4 (within the limits of error) . Asbestos fiber was again used as carrier. We tried out several methods for the preparation of an active tungstic oxide. Dehydration of tungstic acid by calcination in an open crucible at temperatures of 300, 400, 500, 600, and 700° did not yield an active preparation. We then attempted to prepare an active oxide by way of ammonium tungstate. The tungstic acid was dissolved by treatment with an excess of hot concentrated ammonia, the solution evaporated to dryness in a porcelain cup and the resultant white crystals decomposed to WO_3 by heating for 2 hours with access of air. The resultant WO_3 powder had a canary-yellow color. Samples calcined at 500-700° had little activity, and subsequently we limited ourselves to the standard calcination temperature of 450°.

Tests for catalytic activity were performed in a flow apparatus [3], using a flow rate of 10 liters/hour. The duration of contact τ was 0.1 minute. In order to secure reaction velocities that were convenient for observation, it was necessary to use considerably higher concentrations of tungstic oxide on asbestos than was the case for magnesium-chromium catalysts owing to the lower activity of WO_3. In Table 2 are shown values of the velocity constant of isooctane oxidation at various temperatures as a function of the WO_3 content of the asbestos.

As shown by Table 2 and Fig. 3, a linear dependence of the velocity constant, calculated according to the first order equation (2), on the catalyst concentration is maintained only approximately up to a WO_3 content of 60% by weight. Consequently, in order to obtain values of the specific velocity constant which would be comparable with the

TABLE 2

Dependence of the Velocity Constant of Isooctane Oxidation on the Catalyst Content of the Asbestos

Concentra- tion, wt.%.	Values of K at temperatures of:			
	320°	350°	420°	450°
20	0.018	0.029	0.047	0.093
50	0.021	0.055	0.142	0.220
60	0.035	0.069	0.148	0.230
90	0.034	0.066	0.215	0.209

TABLE 3

Activation Energies, Exponential Factors, and Velocity Constants of the Oxidation of Isooctane over Tungstic Oxide + NaOH

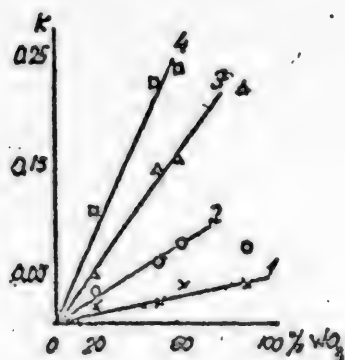| Concentration on asbestos, wt. %	Concentration of NaOH, wt. %	Temperature	Mean value of K_1	$K_{spec.}$	$\log K_0$	E (cal/mole)
50	0	320	0.029	$0.58 \cdot 10^{-3}$	1.3	12400
		340	0.031	$0.62 \cdot 10^{-3}$		
		350	0.054	$1.08 \cdot 10^{-3}$		
		360	0.069	$1.38 \cdot 10^{-3}$		
		390	0.090	$1.80 \cdot 10^{-3}$		
		420	0.142	$2.84 \cdot 10^{-3}$		
		440	0.162	$3.34 \cdot 10^{-3}$		
		450	0.220	$4.40 \cdot 10^{-3}$		
50	0.25	280	0.0090	$0.18 \cdot 10^{-3}$	2.0	14200
		320	0.0305	$0.61 \cdot 10^{-3}$		
		360	0.065	$1.30 \cdot 10^{-3}$		
		380	0.101	$2.02 \cdot 10^{-3}$		
		400	0.130	$2.60 \cdot 10^{-3}$		
		420	0.174	$3.48 \cdot 10^{-3}$		
50	0.75	300	0.065	$1.30 \cdot 10^{-3}$	2.0	15600
		320	0.100	$2.01 \cdot 10^{-3}$		
		340	0.130	$2.60 \cdot 10^{-3}$		
		360	0.198	$3.96 \cdot 10^{-3}$		
50	1.0	300	0.026	$0.52 \cdot 10^{-3}$	3.16	16400
		320	0.0545	$1.09 \cdot 10^{-3}$		
		340	0.080	$1.61 \cdot 10^{-3}$		
		360	0.134	$2.68 \cdot 10^{-3}$		
		380	0.149	$2.98 \cdot 10^{-3}$		
		400	0.200	$4.00 \cdot 10^{-3}$		
		420	0.306	$6.12 \cdot 10^{-3}$		
		440	0.589	$11.68 \cdot 10^{-3}$		
50	1.5	320	0.020	$0.39 \cdot 10^{-3}$	0.5	10900
		360	0.035	$0.70 \cdot 10^{-3}$		
		400	0.052	$1.04 \cdot 10^{-3}$		
		420	0.063	$1.27 \cdot 10^{-3}$		
		440	0.078	$1.57 \cdot 10^{-5}$		
50	2.0	280	0.012	$0.24 \cdot 10^{-3}$	-0.1	9100
		340	0.0285	$0.57 \cdot 10^{-3}$		
		360	0.030	$0.60 \cdot 10^{-3}$		
		400	0.043	$0.86 \cdot 10^{-3}$		
		420	0.060	$1.20 \cdot 10^{-3}$		
50	3.0	320	0.022	$0.44 \cdot 10^{-3}$	-0.8	7100
		340	0.026	$0.52 \cdot 10^{-3}$		
		360	0.029	$0.59 \cdot 10^{-3}$		
		400	0.041	$0.82 \cdot 10^{-3}$		
		440	0.053	$1.07 \cdot 10^{-3}$		
50	17.3 (corresponds to Na_2WO_4)	inactive				
0 wt. % WO_3	50% NaOH on asbestos	inactive				
1% NaOH on asbestos		inactive				

Fig. 3. Dependence of the velocity
constant of isooctane oxidation on
the tungstic oxide concentration of
the asbestos.

1-320°; 2-350° 3 420°, 4-450°;

Fig. 4. Effect of additive (NaOH) on
the velocity constant of isooctane
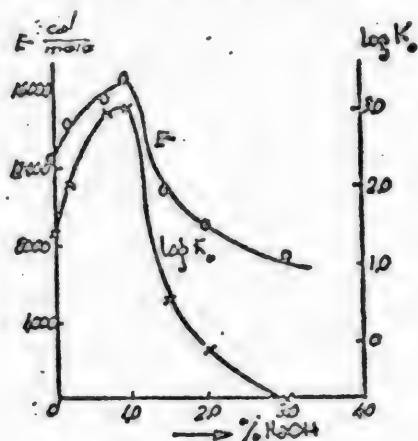oxidation over tungstic oxide.

Fig. 6. Effect of admixture of NaOH
upon the activation energy and logarithm
of the exponential factor of the reac-
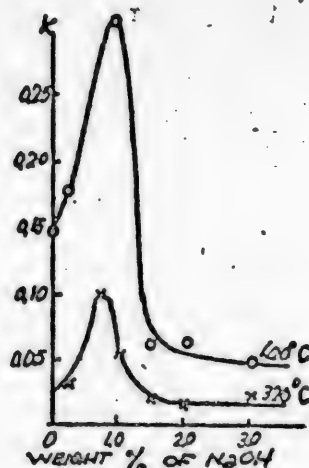tion of complete oxidation of isooctane
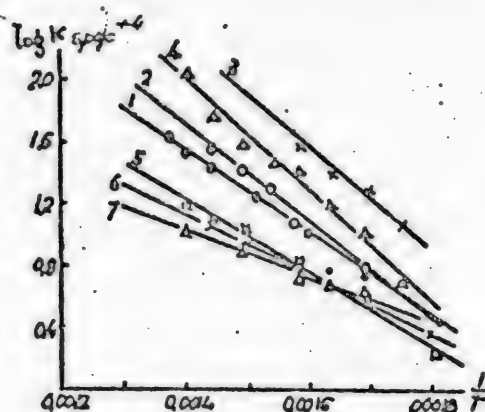over tungstic oxide.

Fig. 5. Dependence of the logarithm
of the velocity constant on the recip-
rocal temperature during oxidation of
isooctane over tungstic oxide with
various contents of NaOH.

1-Pure WO_3; 2 0.25% NaOH 3-0.75%; 4-1.0%;
5-1.5%; 6-2.0%. 7-3.0%

corresponding values in the paper of Margolis and Todes, we subsequently limited
ourselves to a 50% concentration of catalyst on the asbestos.

We also made a study of the effect of addition of NaOH on the catalytic ac-
tivity of WO_3. The alkali was incorporated in proportions of 0.25 to 8% by wt.
of the original catalyst. The method of incorporation consisted in treating the
tungstic oxide with a solution of NaOH of definite concentration before trans-
ferring the catalyst on to the asbestos. Results of the investigation are pre-
sented in Table 3. In all cases the reaction was first order, and the velocity
constant was therefore calculated from equation (2).

The maximum variations in the calculated values of K_O for weakly active

catalysts were 15-20%. This arises from the circumstance that in the investiga-
ted temperature range of 280-440°, the absolute magnitude of the percentage oxid-
ation of isooctane is low (from 0 to 15%). We were unable to raise the reaction
temperature above 440° because at this temperature tungstic oxide admixed with
NaOH completely and irreversibly lost its activity. Moreover, the activity of
some catalysts (for example, WO_3 containing 0.75% NaOH) fell off slightly with
prolonged use.

Fig. 4 shows the dependence of the velocity constant of isooctane oxidation
on the NaOH content of the catalyst. A pronounced maximum is observed at a con-
tent of 0.75-1 per cent by weight of NaOH (calculated on the weight of WO_3).

Fig. 5 shows the dependence of the logarithm of the velocity constant on the
reciprocal temperature. The plots indicate that the data fit Arrhenius straight
lines.

Fig. 6 gives plots of activation energy and logarithm of exponential factor
versus content of additive. The sharp maximum at a content of 0.75-1% NaOH re-
sembles the corresponding maxima for chromite catalysts [1]. The diagram also
demonstrates the concurrent changes in E and K_0 previously noted. This is also
clearly shown in Fig. 7 in which the abscissas are activation energies and the
ordinates are the logarithms of the exponential factors.

All of the results enumerated demon-
strate that in the present case we are
dealing with a clearly defined modifica-
tion effect which fits in perfectly with
the criterion of modification specified
by S.Z.Roginsky in the investigation
cited above. The observed phenomena can-
not be correlated either with simple
poisoning or simple promotion. Nor can
the explanation reside in a simple chem-
ical interaction between alkali and tung-
stic oxide, for 1) the addition of NaOH
changes the kinetic characteristics of
WO_3, and 2) catalysts prepared with pure
NaOH or Na_2WO_4 entirely fail to catalyze
the oxidation of isooctane.

It is our pleasant duty to thank
S.Z.Roginsky and O.M.Todes for their
continuous interest in the investigation
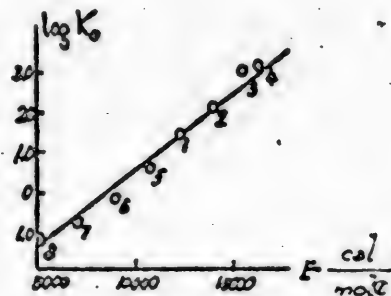and for their valuable advice.

Fig. 7. Dependence of the loga-
rithm of the exponential factor
on the activation energy during
oxidation of isooctane over
tungstic oxide with various con-
tents of NaOH.

1-Pure WO_3; 2-0.25%; 3-0.75% NaOH; 4-1.0%;
5-1.5%; 6-2.0%; 7-3.0%; 8-8.0%.

SUMMARY

1. A study was made of the kinetics of oxidation of ethylene over magnesium
chromium catalyst treated with various proportions of sodium silicate.

2. It was established that during the oxidation of ethylene over treated
magnesium-chromium catalyst the same phenomena of modification were observed as
in the case of oxidation of isooctane over the same catalysts.

3. The kinetics of oxidation of isooctane over tungstic oxide alone and
with admixtures of sodium hydroxide were studied.

4. It is shown that the characteristic features of modification during oxid-
ation of isooctane are also observed with tungstic oxide containing alkali.

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• See CB translation 2053 ff.

EFFECT OF ANHYDROUS FORMIC ACID ON THE STRENGTH OF BASES*

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Formic acid has long attracted the attention of investigators as a solvent. Apart from its pronounced acidic properties, formic acid is characterized by a high dielectric constant and good solvent action. The salt effects in this solvent are considerably smaller than in acetic acid and other solvents with a low dielectric constant.

Schlesinger and co-workers have shown that formic acid possesses a high dissociating action on salts and acids [1]. These studies refuted the erroneous conclusions of Zinninowitch-Tessarin [2] to the effect that association of dissolved acids takes place in formic acid.

Formic acid is a protogenic solvent so that the number of substances developing acid properties in it will be smaller than in water. Conversely, the number of basic substances manifesting acceptor properties for the proton must be greater than in water, the strength of bases in formic acid being equalized. There have been no systematic studies of this aspect and we therefore undertook the present investigation.

EXPERIMENTAL

Formic acid was prepared by distilling the commercially pure acid in vacuum, dehydrating the distillate with boric anhydride for a fortnight, and redistilling in vacuum. Full details of the method are given by Pleskov [3]. The bases used were pure sodium formate, pyridine, benzidine, aniline, β-naphthylamine, α-naphthylamine, glycocoll, caffeine, and theobromine. The purity of the preparations was checked by the melting and boiling points. 0.1 molar solutions of these bases were titrated potentiometrically with an 0.2 molar solution of toluene sulfonic acid which is readily synthesized and dehydrated whereas benzene sulfonic acid, used by Hammett and Dietz [4], introduces serious experimental difficulties owing to its hygroscopicity. Solutions of the bases and acids were prepared with formic acid freshly distilled over boric anhydride.

The quinhydrone electrode was used as the indicating electrode, and the saturated calomel electrode as the comparison electrode. A diagram of the titration vessel is given in Fig. 1. The design is clear from the drawing. Izmailov's lamp potentiometer, details of which have already been published [5], was used. Measurements of the e.m.f. were effected with an accuracy of up to 0.1 mV.

The titration curves are shown in Fig. 2. The abscissas are the percentages of titrated base and the ordinates are the e.m.f. values. The curves show that the weak bases which were examined have differing values of pK in water (pK of pyridine = 8.7; pK of caffeine = 13.4) but the titration in anhydrous formic acid
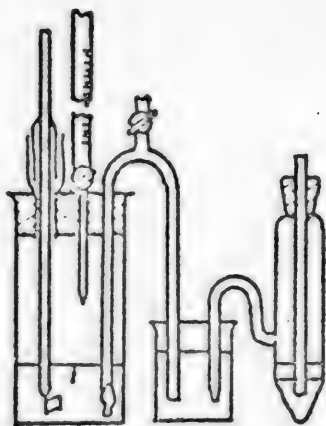
Fig. 1. Titration vessel.

gives identical values. Only the titration curve of benzidine has a larger slope, due to its dibasicity.

For the purpose of quantitative evaluation of the effect of formic acid on the strength of bases, we calculated their dissociation constants, using two methods.

1. Roller's method.[6] $\varepsilon = 200\sqrt{k}\sin h\Delta$, where ε = the previously given titration error in per cent; Δ is the potential drop in millivolts, corresponding to the given titration error; $k = K_1/C_bK_b$, where K_1 is the ionic product of the medium, K_b is the dissociation constant of the base, and C_b is the concentration of the base. In our case $C_b = 0.1$; K_1 is taken from the paper of Hammett and Dietz [4] corresponding to the value pK = 5.65 for 0.13 molar concentration of salt. Having taken the titration error as 1%, we calculated the values of the constant K_b. These values are given in the table (column 3). The pK values of the bases in water are taken from Lurye's book [7].

2. A method of calculating the dissociation constant for the case of titration of acids by displacement has been proposed by Izmailov [8]. This method gives true values of the dissociation constant in the case of strong acids. Bronsted's theory of acids and bases regards acid-base interaction as a binary
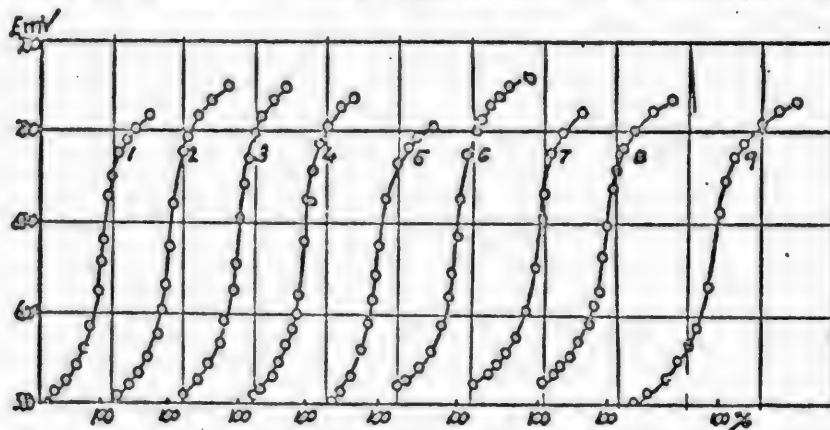

Fig. 2. Titration curves of 0.1 molar solutions of bases with 0.2 molar solutions of toluene sulfonic acid in anhydrous formic acid.

1-Sodium formate; 2-pyridine; 3-aniline; 4-β-naphthylamine; 5-α-naphthylamine; 6-glycocoll; 7-caffeine; 8-theobromine; 9 benzidine.

protolytic equilibrium. The necessity now arises for a revision of nomenclature of reactions. Klages [9] has put forward a new classification of reactions, according to which a reaction involving participation of the solvent in the process of displacement titration, for instance

$$H_3O\cdot ClO_4' + Na_2CO_3 \rightleftarrows NaHCO_3 + Na\cdot ClO_4' + H_2O,$$
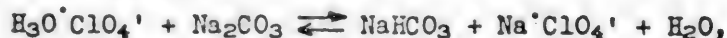
in the usual sense is a neutralization reaction. On this basis we attempted to adapt Izmailov's method to the case of acid-base titration. Utilizing Kolthoff's

Dissociation Constants of Bases in Water and in Formic Acid

Base	pK_{H_2O}	pK_{HCOOH}		$pK_{H_2O} - pK_{HCOOH}$
		Roller's method	Our method	
Sodium formate....	—	2.45	2.38	—
Pyridine..........	8.69	2.45	2.38	5.3
Benzidine.........	9.03;10.25	2.70	2.30	7.9
Aniline	9.40	2.34	2.42	7.0
β-Naphthylamine...	9.89	2.45	2.38	7.5
α-Naphthylamine...	10.08	2.70	2.28	7.8
Glycocoll.........	—	2.45	2.38	—
Caffeine..........	13.39	2.45	2.38	11.0
Theobromine.......	13.89	2.70	2.30	11.5

data [10] for displacement titration of bases, we constructed a curve of the dependence of the potential drop in the vicinity (1%) of the equivalent point on the pK of the base (Fig. 3). Having determined, from the titration curve, the potential drop approximately 1% before or after the equivalent point, with the aid of Fig. 3 one can find the pK of the base. Values of pK determined by this method appear in the fourth column of the table.

As can be seen from the data presented, the pK values of bases in HCOOH calculated by different methods are in substantial agreement. Our method gives slightly lower values, which we are inclined to attribute to the inaccuracy of the value for the ionic product of the solvent which was used in the calculation of the pK of bases by Roller's method.

In our method the accuracy of the values of pK is governed by the accuracy of the values of the potential drop in the vicinity of the equivalent point, and also by the character of its dependence on pK. In the region of interest to us, this dependence is characterized by a curve nearly parallel to the axis of the abscissas, and in this case this does not permit sufficiently reliable results to be obtained.
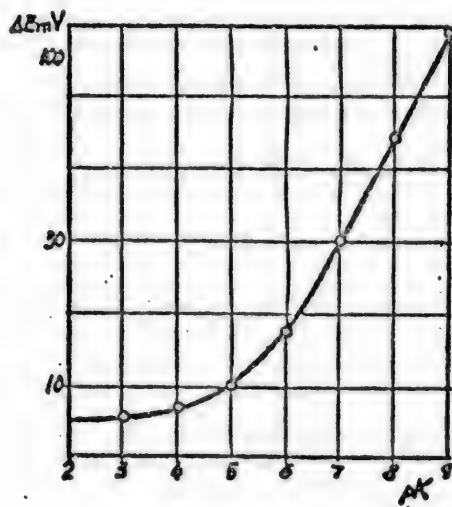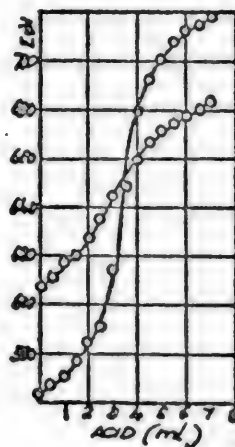

Fig. 3.

Fig. 4.

The results indicate that formic acid equalizes the strength of bases. Weak bases become $10^8 - 10^{11.5}$ times stronger in formic acid. For example, caffeine and theobromine are stronger in this solvent than in water by a factor of several thousand millions. While they are practically neutral in water, these bases behave in formic acid like the strongest possible base (sodium formate).

Izmailov proposed a classification of cases in which the use of non-aqueous solvents improves the conditions of acid-base titrations. In our example, according to this classification, the improvement in the conditions of titration is based on a decrease in the ratio K_1/K_b, for in comparison with water the ionic product of the solvent (K_1) is here reduced at the same time as the basicity (K_b) is increased, whereas in acetic acid, for instance, the ionic product of which is close to the ionic product of water, the improvement in the conditions of titration is caused mainly by the rise in basic strength.

Still another feature of titration in formic acid, and in general in solvents with a low ionic product, must be taken into consideration. The ionic product of formic acid is 10^{-6}, so that the pH scale in this solvent is nearly 8 units less than for water. The neutrality point of solutions in formic acid lies at a pH of 3. Consequently the titration of dilute solutions in solvents with a low ionic product cannot be performed with adequate analytical accuracy, since the potential drop (pH) from the acid region to the neutral region is insufficient. This is well illustrated by Fig. 4 in which is plotted the titration of an 0.1 molar solution of theobromine with an 0.2 molar solution of toluene sulfonic acid (curve 1) and also the titration of an 0.01 molar solution of theobromine with an 0.02 molar solution of toluene sulfonic acid (curve 2) in formic acid. In curve 2 the pH jump from the basic region (0.01) to the neutral one is at the most about 1 pH unit, whereas in aqueous solutions on titration of an 0.01 $\underline{N}$ solution of a strong base the pH drop from the basic (0.01$\underline{N}$) to the neutral region is five pH units.

SUMMARY

A study was made by potentiometric titration of the effect of anhydrous formic acid on the strength of bases. The dissociation constants of a series of bases were calculated from the experimental data. Formic acid equalizes the strength of bases, considerably increasing the strength of weak bases. This enables substances (theobromine, caffeine) which are practically neutral in water to be titrated in formic acid with sufficient analytical accuracy. Attention is drawn to the characteristics of titration in solvents with a low ionic product.

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THE PROBLEM OF THE CLEAVAGE OF RADICALS IN ORGANOMETALLIC COMPOUNDS

OF METALS OF THE FOURTH GROUP

VII. CLEAVAGE OF RADICALS BY THE ACTION OF BISMUTH TRICHLORIDE
ON COMPOUNDS OF THE TYPE OF R_4Me, WHERE Me = Si, Sn, Pb*

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In a previous communication we touched on the problem of radical cleavage by the action of aluminum chloride and iron chloride upon compounds of the type of R_4Me, where Me = Si, Sn, Pb [2].

With the objective of studying more closely the relative stability of the Me—C bond and the role of the cation of the dealkylating agent and the solvent in the dealkylation reaction, we made a series of investigations with bismuth trichloride as the dealkylating agent. Experiments were made both in chloroform as a medium and in the absence of a solvent.

As far as we are aware the literature does not report the use of bismuth trichloride as a dealkylating agent for organometallic compounds of the fourth group.

A. Action of Bismuth Trichloride on R_4Si

1. No visible reaction was detected in preliminary experiments on the interaction of bismuth trichloride with tetrabenzyl silicon both in boiling ether and in boiling alcohol.

2. During the action of one-third mole of bismuth trichloride in a nitrogen stream on 1 mole of tetraethyl silicon at the boiling point of the latter (in the absence of solvent), there was obtained a small yield (23%) of triethyl chlorosilicon. The reaction proceeds according to the equation:

$$(C_2H_5)_4Si + BiCl_3 \longrightarrow (C_2H_5)_3SiCl. \qquad (1)$$
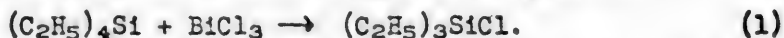
Tetraethyl silicon was synthesized by the previously described method [3]. Bismuth trichloride was prepared from bismuth and concentrated hydrochloric acid and was purified by sublimation.

B. Action of Bismuth Trichloride on R_4Sn

1. Reaction of 1 mole of tetraethyl tin with 2 moles of bismuth trichloride in a chloroform medium in a nitrogen stream yielded triethyl tin chloride (30%) and a small amount (6%) of diethyl tin dichloride. The following reaction course may be assumed:

$$(C_2H_5)_4Sn + BiCl_3 \longrightarrow (C_2H_5)_3SnCl + (C_2H_5)_2SnCl_2. \qquad (2)$$
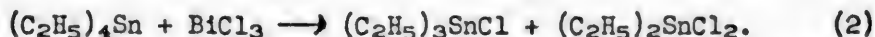
Tetraethyl tin was prepared by the Kocheskov Method [4] as slightly modified by us.

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*Preliminary data were submitted at a session of the Tashkent section of the Mendeleev Society in March 1941 [1].

2. Reaction of 1 mole of tetra-n-butyl tin with 1.3 moles of bismuth trichloride in a nitrogen stream (in the absence of solvent) at 120° proceeded with formation of di-n-butyl tin dichloride (35% of theory):

$$(n-C_4H_9)_4Sn + BiCl_3 \longrightarrow (n-C_4H_9)_2SnCl_2. \qquad (3)$$

3. No visible reaction was observed (in preliminary experiments) in the treatment of bismuth trichloride with tri-n-propyl-n-butyl tin in a medium of boiling ether or boiling alcohol.

4. Reaction of 1 mole of tri-n-propyl-n-butyl tin with 1.7 moles of bismuth trichloride in a nitrogen stream (in the absence of solvent) at 120° proceeds with formation of n-propyl-n-butyl tin dichloride, a substance not previously described in the literature. The yield was 37% of theory:

$$(n-C_3H_7)_3Sn(n-C_4H_9) + BiCl_3 \longrightarrow (n-C_3H_7)(n-C_4H_9)SnCl_2. \qquad (4)$$

We have already [6] described the preparation of tri-n-propyl-n-butyl tin.

C. Action of Bismuth Trichloride on R_4Pb

An experiment was performed with 1 mole tetraethyl lead and 1.3 moles bismuth trichloride in a nitrogen stream (in the absence of solvent), and yielded lead chloride (45% of theory) and triethyl lead chloride (15%):

$$(C_2H_5)_4Pb + BiCl_3 \longrightarrow PbCl_2 + (C_2H_5)_3PbCl. \qquad (5)$$
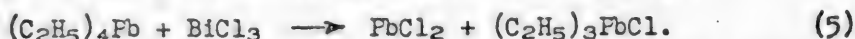
The mechanism of the above reactions and the problem of the formation of organobismuth compounds will be the subject of further investigations.

Our immediate concern is with the dealkylation by bismuth trichloride of aromatic compounds of group 4 metals of the type of Ar_4Me (where Me = Si, Sn, Pb) and of compounds of group 5 metals of the type of Ar_3Me (where Me = As, Sb, Bi).

Further studies in this direction will give us the opportunity of arranging metals in the order of the strength of their bond with a given radical.

EXPERIMENTAL

Action of bismuth trichloride on tetrabenzyl silicon (preliminary experiments). Bismuth trichloride was added to boiling ether and alcohol solutions of tetrabenzyl silicon in separate tests. The mixtures were heated for 2-3 hours on the water bath. In both tests no reaction was observed and the bismuth trichloride and tetrabenzyl silicon were recovered.

Action of bismuth trichloride on tetraethyl silicon in the absence of solvent. Into a round-bottomed flask with a reflux condenser was introduced 13 g (0.09 mole) of tetraethyl silicon and gradual addition was made of 9.4 g (0.03 mole) of bismuth trichloride. No heating of the flask was detected at this stage. The mixture was boiled for 12 hours in a continuous stream of nitrogen. The initial cherry-red color of the boiling liquid gradually changed to brown. After heating for only 2 hours the formation of white crystals was noted in a quantity which increased with further heating. The liquid mass in the reaction flask was extracted with petroleum ether; the crystals did not dissolve and were isolated by suction. The ethereal extract was distilled and yielded a fraction boiling at 139-141° (725 mm) in the amount of 3.1 g. According to Ladenburg [7], the boiling point of triethylsilicon chloride is 143.5° (normal pressure); the composition was confirmed by analysis for silicon. Other fractions contained tetraethyl silicon. The yield of triethyl silicon chloride was 23% of theory (calculated on the tetraethyl silicon). The crystals after sublimation had a melting point of 95°, and ignited in a burner flame. Owing to the small amount,

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*A. V. Yarmakhova collaborated in the experiments.

its composition could not be established.

$$0.1825 \text{ g substance: } 0.0720 \text{ g SiO}_2.$$
Found %: Si 18.41.
$C_8H_{15}SiCl$. Computed %: Si 18.64.

Action of bismuth trichloride on tetraethyl tin in chloroform. To 16 g (0.068 mole) tetraethyl tin dissolved in 20 ml of chloroform there was gradually added, with passage of a continuous nitrogen stream, 42 g (0.133 mole) of bismuth trichloride in a chloroform medium (in an earlier series of experiments [7] we had similarly introduced aluminum chloride [experiments 2, 4, and 7] and iron chloride [experiments 8, 9, and 11] in a chloroform medium). The reaction mass became slightly warm. On the following day the mixture was heated for 3 hours on the water bath. The chloroform was distilled off. The residue was treated with water and worked up with petroleum ether. The ether layer was separated off, dried over calcium chloride, and distilled. A fraction boiling at 200-205° (735 mm) was obtained. According to Cahours [8] the boiling point of triethyl tin chloride is 208-210° (normal pressure); according to Kocheshkov [9] it is 209-211° 753 mm). The yield of triethyl tin chloride was 5 g (30.4%).

$$0.3760 \text{ g substance: } 0.2368 \text{ g SnO}_2.$$
Found %: Sn 49.50.
$C_8H_{15}SnCl$. Computed %: Sn 49.22.

A higher boiling fraction, 215-225°, eventually crystallized. After two recrystallizations from ligroin a substance was isolated which melted at 84°. According to Pfeiffer [10] and Kocheshkov [11] diethyl tin dichloride melts at 84°. A mixture of the substance with authentic diethyl tin dichloride did not cause any depression in the melting point. Yield 1 g (6% of theory).

Action of bismuth trichloride on tetra-n-butyl tin in absence of solvent. To 10 g (0.029 mole) tetra-n-butyl tin in a continuous stream of nitrogen there was gradually added 12 g (0.038 mole) of bismuth trichloride. The slightly darkening reaction mixture was heated on an oil bath at a bath temperature of 120-130° for 6 hours. On standing at room temperature, crystals separated out and after one recrystallization from ligroin they melted at 44-45°. Pfeiffer [10] gives 43° as the melting point of di-n-butyl tin dichloride. Yield 3 g (34.5% of theory).

$$0.1475 \text{ g substance: } 0.0724 \text{ g SnO}_2.$$
Found %: Sn 38.65.
$C_8H_{18}SnCl_2$. Computed %: Sn 39.09.

Action of bismuth trichloride on tri-n-propyl-n-butyl tin in a solvent. In preliminary experiments in boiling ether and boiling alcohol no reaction was observed. The original materials were apparently recovered.

Action of bismuth trichloride on tri-n-propyl-n-butyl tin in absence of solvent. To 4 g (0.13 mole) tri-n-propyl-n-butyl tin was added 7 g (0.022 mole) bismuth trichloride and the mixture was heated for 2 hours in a nitrogen stream on the oil bath, the temperature of which was 120-130°. On standing at room temperature the contents of the flask crystallized. After a single recrystallization from petroleum ether the product melted at 67-68°. It was soluble in alcohol, and gave a positive reaction for chlorine and tin. Judging by the tin analysis it corresponds to the hitherto undescribed n-propyl-n-butyl tin dichloride. Yield 1.4 g (37% of theory).

$$0.2810 \text{ g substance: } 0.1452 \text{ g SnO}_2.$$
$$0.3426 \text{ g substance: } 0.1774 \text{ g SnO}_2.$$
Found %: Sn 40.72, 40.78.
$C_7H_{16}SnCl_2$. Computed %: Sn 40.98.

Action of bismuth trichloride on tetraethyl lead in absence of solvent. 10 g (0.031 mole) tetraethyl lead was placed in a round-bottomed flask fitted with a reflux condenser and addition was made over a period of an hour of 13 g (0.041 mole) of bismuth trichloride in a nitrogen stream. Considerable heat was developed. The mixture was left overnight. By the next day, crystals had settled out. After treatment with boiling ether, when a small proportion went into solution, the main bulk of crystals was dissolved in hot water. On cooling the aqueous solution, crystals separated out which gave the characteristic reactions of lead chloride, and the identity of the latter was confirmed by quantitative analysis. Yield 3.9 g lead chloride (45.8% of theory).

$$0.1824 \text{ g substance: } 0.1983 \text{ g } PbSO_4.$$
$$\text{Found \%: Pb } 74.28;$$
$$PbCl_2. \text{ Computed \%: Pb } 74.50.$$

Crystals separated from the ether solution on standing and were in the form of long needles which became slightly colored at 118-120° and possessed an odor irritating to the mucous membrane. The lead analysis indicates that it is triethyl lead chloride. Yield 1.5 g (15% of theory).

$$0.1844 \text{ g substance: } 0.1690 \text{ g } PbSO_4.$$
$$\text{Found \%: Pb } 62.64.$$
$$C_6H_{15}PbCl. \text{ Computed \%: Pb } 62.85.$$

SUMMARY

1. It is shown that bismuth trichloride can serve as a dealkylating agent in reactions with compounds of the type of R_4Me (where Me = Si, Sn, Pb) in a similar manner to mercuric chloride [3], aluminum chloride, and iron chloride [2] which we had previously investigated.

2. In its chemical activity as a dealkylating agent, bismuth trichloride is considerably inferior to aluminum chloride and resembles iron chloride and mercuric chloride.

3. Dealkylation proceeds with cleavage of the lighter radical.

4. Dealkylation with bismuth trichloride apparently does not require the use of a solvent. An important factor is the temperature, a higher temperature being required with increasing complexity of the radical.

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ACETYLENE DERIVATIVES

120. MECHANISM OF HYDRATION AND CYCLIZATION OF DIENYNES.

XXVII. CONVERSION OF 2-METHYL-1-VINYLETHYNYLCYCLOHEXAN-1-OL INTO 1,8-DIMETHYL-Δ^1-HEXAHYDROINDEN-3-ONE.

A NEW SYNTHESIS OF POLYCYCLIC KETONES CONTAINING THE CYCLOPENTANONE RING WITH ANGULAR SUBSTITUENTS
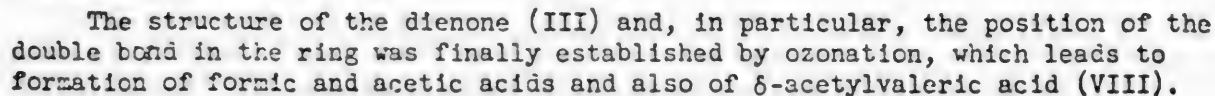
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In previous communications from our laboratory it was shown that hydration of 1,1-disubstituted dienynes yields the corresponding substituted dienones (vinylallyl ketones) which undergo cyclization with extraordinary ease into the gem-substituted cyclopentenones [1,2,3].

$$R = CH_3, \ (CH_3)_2CH, \ C_6H_5.$$
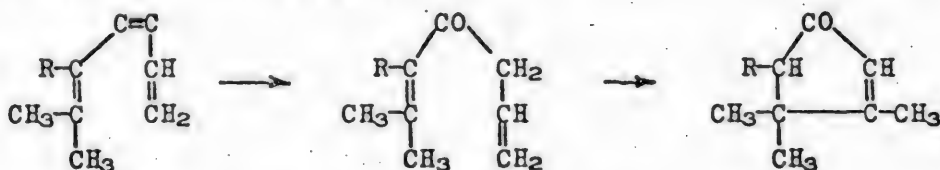
Hence, the cyclization of substituted vinylallyl ketones does not call for the presence of free hydrogen in the vinyl radical of these ketones, and the cyclization in question may be also successfully effected (and even more readily) at the expense of the hydrogen atoms of the allyl group. The application of these reactions to the cyclization of dienynes, the substituted vinyl group of which enters the ring system, must lead to the formation of polycyclic ketones containing the cyclopentanone ring with angular substituents. As the starting material for our projected investigation we selected the more accessible o-methyl-cyclohexanone, condensation of which with vinylacetylene in presence of powdered potassium hydroxide gave 2-methyl-1-vinylethynyl cyclohexan-1-ol in a yield of 93%, while dehydration of the latter with the aid of 50% sulfuric acid gave 2-methyl-1-vinylethynyl-Δ^1-cyclohexene (II) in about 90% yield. The latter is the simplest cyclic dienyne with the desired structure. During hydrogenation in presence of Pt catalyst, the carbinol (I) takes up 3 molecules of hydrogen to form 2-methyl-1-butylcyclohexan-1-ol (V), while the dienyne (II) takes up 4 molecules of hydrogen during hydrogenation and gives 1-methyl-2-butylcyclohexane (VI). It should be noted that addition of the first three molecules of hydrogen to the dienyne (II) proceeds very quickly, but the fourth molecule, which attaches itself to the double bond in the ring, is taken up slowly.

The dienyne (II) is completely hydrated when heated in aqueous solutions of methanol in presence of mercuric sulfate and forms allyl-2-methyl-Δ^1-cyclohexenyl

OH
|
C₄H₉
CH₃
(V)

C₄H₉
CH₃
(VI)

—COC₃H₇
CH₃
(VII)

COOH(CH₂)₄COOH
NaBrO
CH₃CO(CH₂)₄COOH
(VIII)

3H₂, Pt   4H₂, Pt   2H₂, Pt   O₃

OH
|
C
‖
C
|
CH₃ CH
      |
      CH₂
(I)

50% H₂SO₄
50-60°

C
‖
C
|
CH₃ CH
      |
      CH₂
(II)

95% CH₃OH
H₂SO₄

CO
|
CH₂
|
CH₃ CH
      |
      CH₂
(III)

CH₃OH
C₇H₇SO₃H

CO
|
CH₂
|
CH   CHOCH₃
      |
      CH₃
(IV)

H₃PO₄   H₃PO₄   H₃PO₄

O
CH₃
CH₃
(X)

H₂, Pt

O
CH₃
CH₃
(IX)

O₂

—COOH
—COCH₃
CH₃
(XI)

NaBrO

—COOH
—COOH
CH₃
(XII)

H₂, Pt

CH₂
‖
CH
|
CH
‖
CH₂
+
CH—CO
‖   O
C—CO
|
CH₃
(XIII)

CO
CO
O
CH₃
(XIV)

COOH
COOH
CH₃
(XV)

ketone (III), which under the experimental conditions adds on one molecule of methanol and is partially converted into the methoxyketone (IV). The latter readily splits off methanol when distilled in vacuum in presence of small amounts of p-toluene sulfonic acid to form the dienone (III). Hydrogenation of the latter in presence of Pt catalyst in alcoholic solutions is accompanied by the uptake of only one molecule of hydrogen and only one allyl group is hydrogenated, the double bond in the ring remaining unattacked, whereas in glacial acetic acid solution the dienone (III) undergoes complete hydrogenation to propyl-2-methyl-cyclohexyl ketone (VII). A similar effect of substitution on the velocity of hydrogenation of the double bond in the ring has also been repeatedly observed in earlier studies [4,5,6].

The structure of the dienone (III) and, in particular, the position of the double bond in the ring was finally established by ozonation, which leads to formation of formic and acetic acids and also of δ-acetylvaleric acid (VIII).

Oxidation of the latter with bromine-alkali yielded adipic acid. As was to be expected, the dienone (III) is completely cyclized in presence of phosphoric acid according to the foregoing scheme and forms 1,8-dimethyl-Δ^1-hexahydroinden-3-one (IX) in about 90% yield. The latter contains an angular methyl group. The indenone (IX) is also obtained directly in about 60% yield from the dienyne (II) as well as from the carbinol (I) by treatment with phosphoric acid. In the latter case, all three reactions – dehydration of the carbinol (I), hydration of the dienyne (II), and cyclization of the dienone (III) – are effected in a single operation without separation of intermediate products. Hydrogenation of the indenone (IX) with Pt catalyst in alcohol or glacial acetic acid solution is accompanied by the uptake of one molecule of hydrogen when 1,8-dimethylhexahydroindan-3-one is smoothly formed (X). The structure of the indenone (IX) was conclusively demonstrated by ozonation which yielded 2-methyl-2-acetylcyclohexane carboxylic acid (XI). Oxidation of the latter with bromine-alkali then gave 1-methylhexahydrophthalic acid (XII). This acid did not depress the melting point of the synthetic product obtained by condensing citraconic anhydride (XIII) with butadiene, hydrolyzing the anhydride (XIV) to 1-methyl-Δ^3-tetrahydrophthalic acid, and hydrogenating the latter in the presence of Pt catalyst.

The above-described indenone (IX) is obtained in the form of two geometrical isomers giving two dinitrophenylhydrazones (m.p.s 175 and 184°) and only one semicarbazone, which is probably explained by cis-trans isomerization at the instant of its formation:
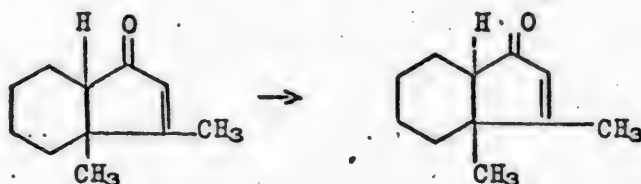

This isomerization takes place with particular ease in presence of sodium methylate, as was shown by our laboratory in a whole series of similar cases [8].

The indanone (X) was likewise obtained in two isomeric forms which were recovered unchanged after treatment with sodium methylate. In this case the geometrical isomerism is complicated by the influence of the methyl group in the 1-position and by the possibility of development of a new series of stereoisomers:
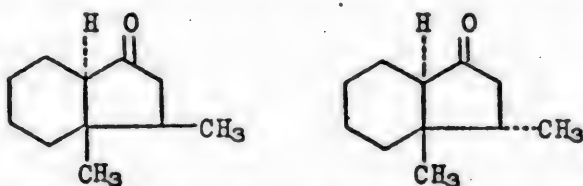

The possibility is not excluded that during dehydration of the carbinol (I) a very small amount of the dienyne (XVI) may be formed, the hydration and cyclization of which might yield 1,4-dimethyl-$\Delta^{8,9}$-tetrahydroindan-3-one (XVIII):

(XVI)　　　　　　(XVII)　　　　　　(XVIII)
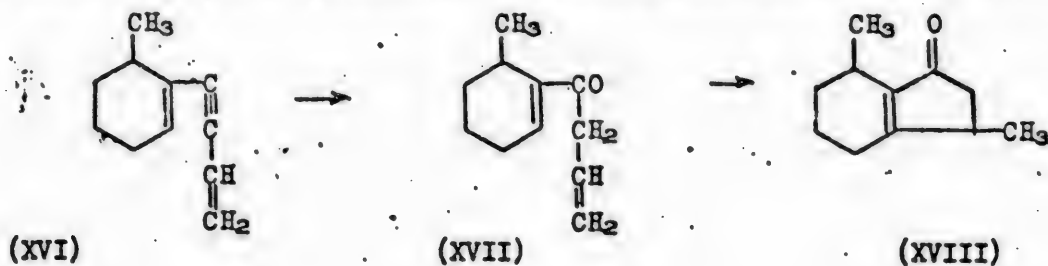
Although the data of hydrogenation and ozonation have indisputably established that the indenone (IX) is the predominating product among the cyclic ketones, there still remains the possibility of the presence of very small admixtures of the indenone (XVIII), and this to an even greater degree complicates the picture of the isomerization of the compounds described in this paper.

It is interesting to note that the ratio of the isomers in the cyclic ketones obtained by cyclization of the dienone (III) and by direct cyclohydration of the dienyne (II) is not perfectly identical.

An important fact emerging from this investigation is that hydration and cyclization of dienynes constitutes a remarkably easy route to polycyclic compounds containing the cyclopentanone ring with angular substituents. This is of great interest in relation to the problem of synthesis of sterols:
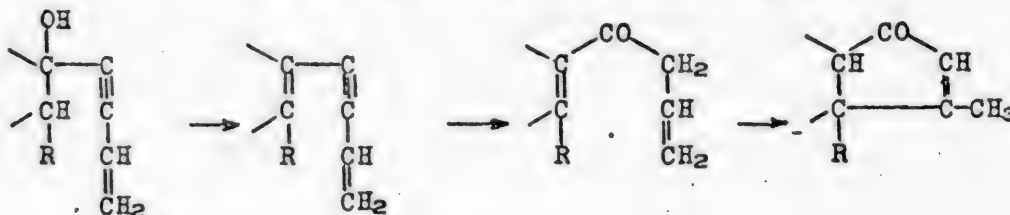
It should again be emphasized that the above transformations can be realized with high yields (60-70% at all three stages) in one operation by treatment of vinylethinylcarbinols with phosphoric acid.

EXPERIMENTAL

Condensation of o-methylcyclohexanone with vinylacetylene. 100 ml dry ether and 47 g powdered potassium hydroxide were placed in a flask. Then, with cooling by iced water and with agitation, a solution of 73 g of o-methylcyclohexanone and 50 g of vinylacetylene in 150 ml of ether was added drop by drop in the course of an hour. Following the addition of the reagents, the reaction mass was stirred at 0° for 5 hours and left overnight at room temperature. The next day the alkali was washed out with water (150 ml), the product neutralized with 10% hydrochloric acid, dried with sodium sulfate and distilled in vacuum. There was obtained 97 g of 2-methyl-1-vinylethynylcyclohexan-1-ol (I) with b.p. 76.5° (2.5 mm); n_D^{17} 1.5110 [9]. Yield 91%.

Hydrogenation of 2-methyl-1-vinylethynylcyclohexan-1-ol. 5.2 g of the substance dissolved in 20 ml of methanol was hydrogenated in presence of Adams' Pt catalyst. Over a period of 3.5 hours 2,260 ml of hydrogen were absorbed as compared with the theoretical requirement of 2,500 ml. The catalyst was filtered off, the methanol distilled off on the water bath, and the residue distilled in vacuum. There was obtained 5.1 g of 1-butyl-2-methylcyclohexan-1-ol (V) [10] in the form of a colorless, transparent, mobile liquid with a pleasant odor.

B.p. 72-72.5° (3.5 mm); n_D^{20} 1.4692; d_4^{20} 0.9081; MR found 52.15, computed 52.32.

4.930 mg substance: 13.957 mg CO_2; 5.645 mg H_2O.
5.700 mg substance. 16.112 mg CO_2; 6.625 mg H_2O.
Found %: C 77.26; 77.14; H 12.81, 13.00
$C_{11}H_{22}O$. Computed %: C 77.65; H 12.94.

Dehydration of 2-methyl-1-vinylethynylcyclohexan-1-ol. A mixture of 95.6 g of 2-methyl-1-vinylethynylcyclohexan-1-ol (I) and 90 g of 50% sulfuric acid was agitated for one hour at 40°, for one hour at 50°, and for 3 hours at 60°. The product was extracted with ether, washed with sodium carbonate solution, dried

with sodium sulfate, and distilled in vacuum. There was obtained 75 g of 2-methyl-1-vinylethynyl-Δ^1-cyclohexene (II):

B.p. 65° (3.5 mm); n_D^{20} 1.5430; d_4^{20} 0.8947; MR found 51.44, computed 47.86.

3.219 mg substance: 10.696 mg CO_2; 2.675 mg H_2O.
Found %: C 90.56; H 9.30.
$C_{11}H_{14}$. Computed %: C 90.41; H 9.59.

2-Methyl-1-vinylethynyl-Δ^1-cyclohexene (II) is a colorless mobile liquid with the characteristic odor of the hydrocarbons of the vinylacetylene series, rapidly turning yellow and polymerizing when kept. Polymerization is inhibited by addition of a small quantity of pyrogallol.

Hydrogenation of 2-methyl-1-vinylethynyl-Δ^1-cyclohexene. 4.6 g of the substance dissolved in 20 ml of glacial acetic acid was hydrogenated in presence of Pt catalyst. During the first hour of hydrogenation 2.5 liters of hydrogen were absorbed, after which the hydrogenation slowed down considerably so that in the subsequent 12 hours 335 ml hydrogen in all were absorbed. The total absorption was thus 2,835 ml as against the theoretical requirement of 2,820 ml hydrogen. At the conclusion of the hydrogenation the product was floating on the surface as an oil. The catalyst was filtered off, the acetic acid neutralized with a 20% solution of sodium hydroxide, the product extracted with ether, dried with sodium sulfate and distilled in vacuum. There was obtained 4.3 g of 1-butyl-2-methylcyclohexane (VI) in the form of a colorless mobile liquid with a characteristic odor:

B.p. 72-73° (11.5 mm); n_D^{20} 1.4472; d_4^{20} 0.8145; MR found 50.54; computed 50.79.

11.27 mg substance: 35.54 mg CO_2; 14.32 mg H_2O.
Found %: C 86.06; H 14.22.
$C_{11}H_{22}$. Computed %: C 85.71; H 14.28.

Cyclohydration of 2-methyl-1-vinylethynyl-Δ^1-cyclohexene. A mixture of 20 g of the dienyne (II) and 20 ml of phosphoric acid (sp. gr. 1.76) was stirred for 6 hours at 60-65°. The product was diluted with an equal volume of water, extracted with ether, neutralized with soda, dried with sodium sulfate and distilled in vacuum. There was obtained 13 g of 1,8-dimethyl-Δ^1-hexahydroinden-3-one (IX) in the form of a colorless transparent liquid with a characteristic odor reminiscent of camphor:

B.p. 83° at 4 mm; n_D^{20} 1.5068; d_4^{20} 0.9974; MR found 48.91, computed 48.14.

5.340 mg substance: 15.720 mg CO_2; 4.621 mg H_2O.
Found %: C 80.28; H 9.68.
$C_{11}H_{16}O$. Computed %: C 80.49; H 9.75.

Its semicarbazone melted at 176.5-177.5° (from methanol).

3.140 mg substance: 0.531 ml N_2 (24°, 739 mm).
3.680 mg substance: 0.621 ml N_2 (23°, 740 mm).
Found %: N 18.90, 18.95.
$C_{12}H_{19}ON_3$. Computed %: N 19.00

On reaction with 2,4-dinitrophenylhydrazine the above described indenone (IX) gives two dinitrophenylhydrazones: one of these forms orange crystals with m.p. 184-184.5° (from a mixture of benzene and methanol).

4.710 mg substance: 0.661 ml N_2 (23°, 754 mm).
3.504 mg substance: 0.505 ml N_2 (24°, 750 mm).
Found %: N 16.06, 16.35.
$C_{17}H_{18}O_4N_4$. Computed %: N 16.37.

The other dinitrophenylhydrazone separated in the form of crimson-colored

crystals melting at 175-175.5° (from a mixture of benzene and methanol).

$$5.050 \text{ mg substance: } 0.710 \text{ ml } N_2 \text{ (}21°\text{, } 759 \text{ mm}\text{)}.$$
$$5.030 \text{ mg substance: } 0.729 \text{ ml } N_2 \text{ (}21°\text{, } 751 \text{ mm}\text{)}.$$
$$\text{Found \%: N } 16.30, 16.36.$$
$$C_{17}H_{18}O_4N_4. \text{ Computed \%: N } 16.37.$$

The presence of two dinitrophenylhydrazones evidently indicates the existence of cis- and trans-isomers of the indenone (IX). On the other hand the formation of only one semicarbazone may be explained by the isomerization of the cis form of the cyclic ketone into the trans form in the process of formation of the semicarbazone, a phenomenon that has been frequently observed in our laboratory, as well as by other authors [8,12,13].

Hydrogenation of 1,8-dimethyl-Δ^1-hexahydroinden-3-one. 5.2 g of the above-described indenone (IX) was hydrogenated in solution in 25 ml of glacial acetic acid in the presence of platinum oxide. After 3 hours 830 ml of hydrogen had been absorbed as against the theoretical requirement of 785 ml for hydrogenation of one double bond. The acetic acid was distilled off in a low vacuum, the residue dissolved in ether, washed with soda solution, dried with sodium sulfate, and distilled. There was obtained 4.2 g of 1,8-dimethylhexahydroindan-3-one (X), a colorless, mobile liquid with a characteristic odor of turpentine:

B.p. 74-75° (3.5 mm); $n_D^{20}1.4800$; d_4^{20} 0.9763; MR found 48.30, computed 48.60.

$$4.952 \text{ mg substance: } 14.373 \text{ mg } CO_2; 4.767 \text{ mg } H_2O.$$
$$5.518 \text{ mg substance: } 16.054 \text{ mg } CO_2; 5.361 \text{ mg } H_2O.$$
$$\text{Found \%: C } 79.21, 79.40; \text{ H } 10.77, 10.87.$$
$$C_{11}H_{18}O. \text{ Computed \%: C } 79.45; \qquad \text{H } 10.92.$$

Its semicarbazone melts at 195.5-196° (from methanol).

$$3.617 \text{ mg substance: } 0.608 \text{ ml } N_2 \text{ (}25°\text{, } 745 \text{ mm}\text{)}.$$
$$2.533 \text{ mg substance: } 0.428 \text{ ml } N_2 \text{ (}25°\text{, } 746 \text{ mm}\text{)}.$$
$$\text{Found \%: N } 18.85, 19.00.$$
$$C_{12}H_{23}ON_3. \text{ Computed \%: N } 18.84.$$

With 2,4-dinitrophenylhydrazine the indanone (X) also forms two dinitrophenylhydrazones. One is in the form of light-orange crystals melting at 155.5-156° (from a mixture of methanol and benzene).

$$4.585 \text{ mg substance: } 0.639 \text{ ml } N_2 \text{ (}22°\text{, } 764 \text{ mm}\text{)}.$$
$$4.690 \text{ mg substance: } 0.662 \text{ ml } N_2 \text{ (}24°\text{, } 749 \text{ mm}\text{)}.$$
$$\text{Found \%. N } 16.21, 15.99.$$
$$C_{17}H_{20}O_4N_4. \text{ Computed \%: N } 16.28.$$

The other forms crimson-colored crystals with m.p. 122.5-123° (from a mixture of methanol and benzene).

$$4.775 \text{ mg substance: } 0.696 \text{ ml } N_2 \text{ (}22°\text{, } 730 \text{ mm}\text{)}.$$
$$\text{Found \%: N } 16.20.$$
$$C_{17}H_{20}O_4N_4. \text{ Computed \%: N } 16.28.$$

A specimen of a mixture of these two dinitrophenylhydrazones melts at 129-130°.

1,8-Dimethyl-Δ^1-hexahydroinden-3-one also readily hydrogenates in alcohol, forming a substance with the same constants as the one formed by hydrogenation in acetic acid.

Ozonation of 1,8-dimethyl-Δ^1-hexahydroinden-3-one. Into a solution of 8.1 g of the above-described indenone (IX) in 35 ml of chloroform there was passed ozonized oxygen for 14 hours with a velocity of 4.5-5 liters/hour (ozone concen-

tration 6%). The solution of the ozonide was agitated with 80 ml of water for two hours at room temperature. Addition was then made of 15 ml of 30% hydrogen peroxide and the agitation continued for a further 6 hours at 60°. The acids were neutralized with soda (6 g), and the neutral products extracted with ether, but there were hardly any of these present. Analysis of a sample of the aqueous solution of the salts by the calomel method gave 0.35 g formic acid (15.5% of the theoretical yield). A test for acetic acid gave a negative result. The alkaline solution of the salts was evaporated to dryness, the residue worked up with concentrated hydrochloric acid (15 g), the organic acids carefully extracted with ether and the ether solution dried with sodium sulfate. The ether was distilled off from the residue of acids, and then under a pressure of 105 mm at 43-51° there was collected about 0.2 g of formic acid (calomel test). The residue of partially crystallizing yellow oil (6.3 g) was digested with active carbon in water. After filtration and subsequent recrystallization of the separated crystals from water, there was obtained 2 g of pure 2-methyl-2-acetylcyclohexane carboxylic acid (XI), melting at 92.5-93°.

9.943 mg substance: 5.41 ml 0.01 $\underline{N}$ NaOH.
3.285 mg substance: 1.84 ml 0.01 $\underline{N}$ NaOH.
Found: M 183.7, 178.8.
$C_{10}H_{16}O_3$. Computed: M 184.

6.160 mg substance: 14.769 mg CO_2; 4.843 mg H_2O.
10.65 mg substance: 25.34 mg CO_2; 8.51 mg H_2O.
Found %: C 65.44, 64.93; H 8.80, 8.93.
$C_{10}H_{16}O_3$. Computed %: C 65.22; H 8.70.

The semicarbazone of the acid formed melted at 167° (from alcohol).

2.940 mg substance: 0.452 ml N_2 (23°, 744 mm).
3.140 mg substance: 0.484 ml N_2 (23°, 741 mm).
Found %: N 17.36, 17.33.
$C_{11}H_{19}O_3N_3$. Computed %: N 17.43.

Oxidation of 2-methyl-2-acetylcyclohexane carboxylic acid with bromine and alkali. To a solution of 0.2 g of 2-methyl-2-acetylcyclohexane carboxylic acid (XI) in 4 ml of 10% sodium hydroxide was added 0.5 g bromine (the theoretical requirement is 0.52 g) drop by drop while cooling with iced water and while stirring. A white milky precipitate was formed and bromoform separated out in the form of a yellow oily drop. The mixture was agitated for 3.5 hours in the cold and for 2 hours at room temperature. Distillation of the reaction mass in a vacuum of 110-90 mm yielded water together with oily drops of bromoform. It was not possible to isolate the long silvery needlets which solidified in the condenser. The residue of salts was treated with concentrated hydrochloric acid (7 ml), the organic acids were extracted with ether, and the ether extract washed with a little 1% solution of hyposulfite and then with water, and dried with sodium sulfate. After distilling off the solvent, the residual crystals of 1-methylhexahydrophthalic acid (XII) in a quantity of 0.1 g were washed with ether and dried in the air. Melting point 152°. After recrystallization from water the m.p. was unchanged.

3.489 mg substance: 3.7 ml 0.01 $\underline{N}$ NaOH.
3.754 mg substance: 3.87 ml 0.01 $\underline{N}$ NaOH.
Found: M 188.6, 193.8.
$C_9H_{14}O_4$. Computed: M 186.

4.312 mg substance: 9.186 mg CO_2; 2.893 mg H_2O.
4.088 mg substance: 8.723 mg CO_2; 2.778 mg H_2O.
Found %: C 58.14, 58.23; H 7.51, 7.60.
$C_9H_{14}O_4$. Computed %: C 58.06; H 7.52.

The acid so prepared did not depress the melting point of a synthetic specimen of 1-methylhexahydrophthalic acid (m.p. 150°) obtained by condensation of butadiene with citraconic anhydride [14].

Preparation of 1-methylhexahydrophthalic acid. 2.1 g of citraconic anhydride (XIII) (b.p. 101° at 21.5 mm, m.p. 8°; n_D^{22} 1.4690) and 12 ml of a 20% solution of butadiene in benzene were heated in a metal ampulla at 100° for 5.5 hours. At the conclusion of the reaction the benzene was distilled off on the water bath and the residue was fractionated in vacuum. In this manner 1 g of citraconic anhydride was recovered unchanged and 1.1 g of 1-methyltetrahydrophthalic anhydride (XIV) was obtained. B.p. 108-111° at 2.5 mm; n_D^{20} 1.4840. On boiling this anhydride with 3 ml of water for an hour under a reflux condenser, there was formed 1 g of 1-methyltetrahydrophthalic acid (XV), melting at 161° after recrystallization from water. Hydrogenation of 0.8 g of 1-methyltetrahydrophthalic acid (XV) dissolved in 15 ml methanol in presence of Pt catalyst yielded 0.7 g of 1-methylhexahydrophthalic acid (XII), melting at 150° after recrystallization from water.

4.045 mg substance: 8.601 mg CO_2; 2.737 mg H_2O.
4.922 mg substance: 10.478 mg CO_2; 3.392 mg H_2O.
Found %: C 58.03, 58.10; H 7.57, 7.71.
$C_9H_{14}O_4$. Computed %: C 58.06; H 7.52.

Vocke [14] gives 165° as the melting point of 1-methylhexahydrophthalic acid prepared by the above-described method. Linstead and Millidge [16] give 160° as the melting point of cis-methylhexahydrophthalic acid, while Bachmann and Kushner [17] give 214° as the melting point of the trans form.

Hydration of 2-methyl-1-vinylethynyl-Δ^1-cyclohexene. A mixture of 270 g of 93% methanol, 0.4 ml of concentrated sulfuric acid, 40 g of dienyne (II) and 2 g of mercuric sulfate was agitated for 2.5 hours at 60°. Further addition was made, commencing 30 minutes after the start of the reaction, of 2 g of mercuric sulfate in small portions at the rate of 1 g per hour. Following the heating, the catalyst was filtered off, the methanol distilled off in a 90 mm vacuum, and the product neutralized with soda, extracted with ether, dried with sodium sulfate, and fractionated in vacuum. There was obtained 45 g of a mixture of allyl-2-methyl-Δ^1-cyclohexenyl ketone (III) and the corresponding methoxyketone (IV) with b.p. 91-102° at 4 mm; n_D^{10} 1.4970-1.4880. The methoxyketone (IV) was eliminated by distilling the mixture in vacuum in the presence of 0.15 g of p-toluene sulfonic acid (0.3%). Methanol started to distil over at a bath temperature of 130° in a 100 mm vacuum. The yield was 37.7 g of allyl-2-methyl-Δ^1-cyclohexenyl ketone (III) in the form of a yellowish liquid with a characteristic odor:

B.p. 95° at 4 mm; n_D^{20} 1.5062; d_4^{20} 0.9551; MR found 51.03, computed 49.88.

4.428 mg substance. 13.101 mg CO_2; 3.954 mg H_2O.
Found %: C 80.67; H 9.88.
$C_{11}H_{16}O$. Computed %: C 80.49; H 9.75.

Hydrogenation of allyl-2-methyl-Δ^1-cyclohexenyl ketone. 5 g of the freshly distilled dienone (III) in solution in 20 ml of glacial acetic acid was hydrogenated in presence of platinum oxide for 9 hours, about 70% of the theoretical amount of hydrogen being absorbed within the first hour. In all, 1,850 ml of hydrogen was absorbed as against the theoretical requirement of 1,730 ml. The acetic acid was neutralized with 10% sodium hydroxide solution, the product extracted with ether, dried with sodium sulfate and fractionated in vacuum. 2 g of propyl-2-methylcyclohexyl ketone (VII) [7] was isolated in the form of a colorless liquid with a pleasant odor:

B.p. 57° at 3.5 mm; n_D^{20} 1.4520; d_4^{20} 0.8955; MR found 50.61; computed 50.81.

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Citraconic anhydride was prepared from citric acid by the method described by Shriner and co-workers [15].

$$4.161 \text{ mg substance: } 11.976 \text{ mg } CO_2; \ 4.508 \text{ mg } H_2O.$$
$$3.200 \text{ mg substance: } 9.234 \text{ mg } CO_2; \ 3.410 \text{ mg } H_2O.$$
$$\text{Found \%: C } 78.57, \ 78.73; \ H \ 12.11, \ 11.93.$$
$$C_{11}H_{20}O. \text{ Computed \%: C } 78.57; \qquad H \ 11.90.$$

The semicarbazone of propyl-2-methylcyclohexyl ketone melts at 162-163° (re-crystallized from methanol).

$$3.650 \text{ mg substance: } 0.580 \text{ ml } N_2 \ (21°, \ 756 \text{ mm}).$$
$$\text{Found \%: N } 18.35.$$
$$C_{12}H_{23}ON_3. \text{ Computed \%: N } 18.66.$$

During the hydrogenation of allyl-2-methyl-Δ^1-cyclohexenyl ketone in ethyl alcohol, only one molecule of hydrogen is rapidly absorbed and hydrogenation near-ly comes to a standstill. In all probability only one allyl group is hydrogenated, the second double bond in the ring remaining intact. A similar effect of substi-tution on the course of hydrogenation has been repeatedly noted with other com-pounds.

Oxonation of allyl-2-methyl-Δ^1-cyclohexenyl ketone. A stream of ozonized oxygen (ozone concentration 6%) was fed into a solution of 7 g dienone (III) in 30 ml dry chloroform at the rate of 4.5 liters/hour for 20 hours. The ozonide solution was poured into 35 ml water and agitated for 2 hours at room temperature. On the following day 10 ml of 32% hydrogen peroxide was added and the mixture heated on the water bath for 6 hours at 60° and then neutralized with soda (9 g). The chloroform solution was separated, and the aqueous solution extracted with ether, but hardly any neutral product was found. Analysis by the calomel method of a sample (1 ml) of the aqueous solution indicated a total content of 1.087 g formic acid or 55.5% of the theoretical content. The aqueous solution of the salts was evaporated to dryness, the residue treated with concentrated hydro-chloric acid, the acid extracted with ether, and the ether extract dried with sodium sulfate. Removal of the ether on the water bath followed by distillation in a low vacuum yielded 1.2 g of a mixture of formic and acetic acids boiling at 45-52° (80 mm). The presence of formic acid was established by the calomel test, and that of acetic acid by the cacodyl test with arsenious oxide. The partially crystallizing residue of 4.2 g of high-boiling acids was distilled in a higher vacuum: first fraction, b.p. 120-122° at 2.5 mm, n_D^{23} 1.4475 – 1.5 g; second frac-tion, b.p. 122-129° at 2.5 mm, n_D^{23} 1.4505 – 0.3 g; third fraction, b.p. 129-152° at 2.5 mm, n_D^{23} 1.4535 – 0.3 g.

At the conclusion of the distillation the side tube of the flask contained about 0.2 g of yellowish crystals which melted at 133-134°, after recrystalliza-tion from benzene. They were not examined further. All of the three fractions crystallized when placed in freezing mixture, giving acicular white crystals consisting of the known δ-acetylvaleric acid (VIII) in various degrees of pur-ity. The identity of the acid was confirmed by oxidation with bromine-alkali to adipic acid. The first fraction gave a semicarbazone melting at 141.5-142° (re-crystallized from methanol).

$$3.134 \text{ mg substance: } 0.568 \text{ ml } N_2 \ (19°, \ 743 \text{ mm}).$$
$$1.962 \text{ mg substance: } 0.365 \text{ ml } N_2 \ (29°, \ 740 \text{ mm}).$$
$$\text{Found \%: N } 20.71, \ 20.85.$$
$$C_8H_{15}O_3N_3. \text{ Computed \%: N } 20.89.$$

According to the literature [11] δ-acetylvaleric acid semicarbazone melts at 144°.

Oxidation of δ-acetylvaleric acid. To a solution of 1 g of keto acid (VIII) (b.p. 120-122° at 2.5 mm) in 18 ml of 10% sodium hydroxide solution was added 2.5 g bromine drop by drop while cooling with ice water. The mixture was agitated

for three hours (the odor of bromoform was noticed), and the water was then distilled off in vacuum (100 mm). The residue of salts was worked up with 20% hydrochloric acid, the organic acids extracted with ether and the ether extract dried with sodium sulfate. After removal of the ether on the water bath, the solid residue was recrystallized from water (the aqueous solution was first boiled with active carbon to remove resinous impurities). 0.2 g of pure adipic acid, m.p. 149.5°, was obtained. No melting point depression was obtained in admixture with an authentic specimen of adipic acid.

Cyclization of allyl-2-methyl-Δ^1-cyclohexenyl ketone. 11.9 g of the dienone (III) (b.p. 99-101° at 5.5 mm, n_D^{24} 1.5065) and 12 ml of phosphoric acid (sp. gr. 1.765) were mixed for 15 minutes at room temperature and for 6 hours at 60-65°. The product was diluted with water, extracted with ether, neutralized with soda, dried with sodium sulfate, and fractionated in vacuum. There was obtained 10.5 g of the above-described 1,8-dimethyl-Δ^1-hexahydroinden-3-one (IX) in the form of a colorless, transparent liquid with a characteristic camphor-like odor. B.p. 83° at 3.5 mm, n_D^{20} 1.5050; d_4^{20} 0.9984; MR found 48.72, computed 48.14. Reaction of the ketone with semicarbazide hydrochloride yielded two semicarbazones, one melting at 177-178° and not depressing the melting point of the above-described semicarbazone of the product of cyclohydration of the dienyne (II), and the other melting at 202-203° (from methanol) and comprising about 60% of the total.

$$3.838 \text{ mg substance: } 0.661 \text{ ml } N_2 \text{ (24°, 739 mm)}.$$
$$3.004 \text{ mg substance: } 0.511 \text{ ml } N_2 \text{ (24°, 740 mm)}.$$
Found %: N 19.18, 19.04.
$C_{12}H_{19}ON_3$. Computed %: N 19.00.

Reaction of the ketone with 2,4-dinitrophenylhydrazine likewise yielded a mixture of products, but only one dinitrophenylhydrazone could be isolated. This took the form of crimson-colored crystals melting at 175.5-176° (from a mixture of benzene and methanol). It did not depress the melting point of the above described product formed by reaction of dinitrophenylhydrazine with the product of cyclohydration of the dienyne (II).

The 1,8-dimethyl-Δ^1-hexahydroinden-3-one (IX) obtained in this experiment was hydrogenated in presence of Pt catalyst in glacial acetic acid. One molecule of hydrogen was taken up and the product was the above-described 1,8-dimethyl-hexahydroindan-3-one (b.p. 68-69° at 2.5 mm, n_D^{20} 1.4800; d_4^{20} 0.9719), which gave a semicarbazone with m.p. 196-197° and two dinitrophenylhydrazones with m.p.s 155.5-156° and 122.5-123°. These did not depress the melting points of the same derivatives obtained from the hydrogenated product of cyclohydration of the dienyne (II).

The ozonation of 7 g of the above 1,8-dimethyl-Δ^1-hexahydroinden-3-one (IX) yielded a very small amount of formic acid and 5 g of oily, partially crystallizing acids, from which was obtained (after digestion with active carbon and recrystallization from water) 1.5 g of 2-methyl-2-acetylcyclohexane carboxylic acid with m.p. 91° and not depressing the m.p. of the above-described product obtained by ozonation of the product of cyclohydration of the dienyne (II).

Transformation of 2-methyl-1-vinylethynylcyclohexan-1-ol into 1,8-dimethyl-Δ^1-hexahydrinden-3-one. 5 g of 2-methyl-1-vinylethynylcyclohexan-1-ol and 5 ml of phosphoric acid (sp. gr. 1.76) were mixed for 20 minutes at room temperature and for 8 hours at 60-65°. The product was diluted with water, extracted with ether, neutralized with soda, dried and fractionated in vacuum. There was obtained 2.9 g of the above-described 1,8-dimethyl-Δ^1-hexahydroinden-3-one (IX) in the form of a colorless mobile liquid with a characteristic camphor-like odor, b.p. 81° at 3 mm, n_D^{20} 1.5058. Reaction with semicarbazide hydrochloride gave a semicarbazone melting at 178° and not depressing the melting point of the previous specimen.

Treatment of 1,8-dimethyl-Δ^1-hexahydroinden-3-one with sodium methylate.
2.8 g indenone (IX) obtained by cyclohydration of the dienyne (II) and 15 ml of
0.3% solution of sodium methylate were heated together on a water bath under a re-
flux condenser for 3 hours. The product was diluted with water, extracted with
ether, washed with water, dried with sodium sulfate, and fractionated in vacuum.
There was obtained 1.8 g of a substance with b.p. 86-87° at 3.5 mm, n_D^{20} 1.5055,
d_4^{20} 0.9984; MR found 48.72, calculated 48.14. With semicarbazide hydrochloride
a semicarbazone was formed which melted at 178° and did not depress the melting
point of the previously described semicarbazone of the indenone (IX). Two di-
nitrophenylhydrazones were isolated from the mixture resulting from reaction
with 2,4-dinitrophenylhydrazine. One product predominated, having the
form of orange crystals melting at 184.5-185° and not depressing the melting
point of the above-described specimens of the dinitrophenylhydrazones of the
indenone (IX). The other dinitrophenylhydrazone was present in very small amount
in the form of crimson crystals melting at 204-206° (from methanol).

0.410 mg substance: 0.060 ml N_2 (23°, 749 mm).
Found %: N 16.63.
$C_{17}H_{18}O_4N_4$. Computed %: N 16.37.

Similar treatment with sodium methylate of the 1,8-dimethylhexahydroindan-
3-one obtained by hydrogenation of the product of cyclization of dienone (IX) led
to recovery of the starting material unchanged. From the latter were obtained
two dinitrophenylhydrazones melting at 123° and 155° and not depressing the melt-
ing points of the previously described specimens.

SUMMARY

Condensation of vinylacetylene with o-methylcyclohexanone in the presence
of potassium hydroxide results in an over 90% yield of 2-methyl-1-vinylethynyl-
cyclohexan-1-ol (I), dehydration of which with the aid of 50% sulfuric acid gives,
in the same yield, 2-methyl-1-vinylethynyl-Δ^1-cyclohexene (II). When heated in
aqueous methanol solutions in presence of mercuric sulfate, the dienyne (II) is
almost quantitatively hydrated to form allyl-2-methyl-Δ^1-cyclohexenyl ketone
(III), and the latter in presence of phosphoric acid is completely cyclized to
1,8-dimethyl-Δ^1-hexahydroinden-3-one (IX) which contains one angular methyl
group. The indenone (IX) is likewise formed directly in 60-70% yield from the
dienyne (II) and the vinylethynyl alcohol (I) on heating with phosphoric acid.
These transformations constitute a new and very simple synthesis of polycyclic
compounds containing a cyclopentanone ring with angular substituents and may
have great importance for the synthesis of compounds of the sterol group. Hydro-
genation of the unsaturated compounds (I, II, III, and IX) was also effected
in presence of Pt catalyst, yielding the corresponding saturated compounds (V,
VI, VII, and X).

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ACETYLENE DERIVATIVES

121. THE MECHANISM OF HYDRATION AND CYCLIZATION OF DIENYNES.

XXVIII. HYDRATION OF 2,4-DIMETHYL-1-VINYLETHYNYL-Δ¹-CYCLOPENTENE AND THE BEHAVIOR OF THE RESULTANT ALLYL-2,4-DIMETHYL-Δ¹-CYCLOPENTENYL KETONE IN CYCLIZATION REACTIONS

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It has been shown in numerous instances in our laboratory [1] that the substituted vinylallyl ketones formed by hydration of dienynes undergo cyclization to the corresponding cyclopentenones with extraordinary ease and in the majority of cases almost quantitatively under the influence of acids (phosphoric, hydrochloric, and others):
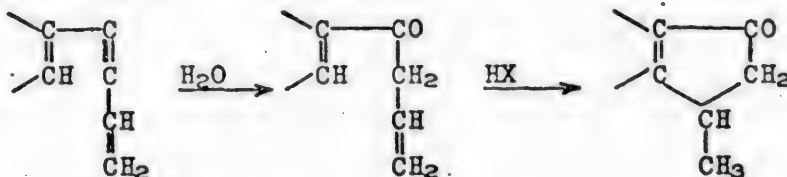

Cyclization, with the aid of phosphoric and hydrochloric acid, of the most diverse substituted vinylallyl ketones of the aliphatic, alicyclic, and aromatic series into the corresponding cyclopentenones usually proceeds with heat development when the reaction is conducted even at room temperature. It is a striking example of the extraordinarily easy transition from open-chain compounds to cyclic systems. The sole exception is allyl-Δ¹-cyclopentenyl ketone which is entirely incapable of undergoing the above-described cyclization but hydrates to the corresponding bicyclic pyrone [2]:
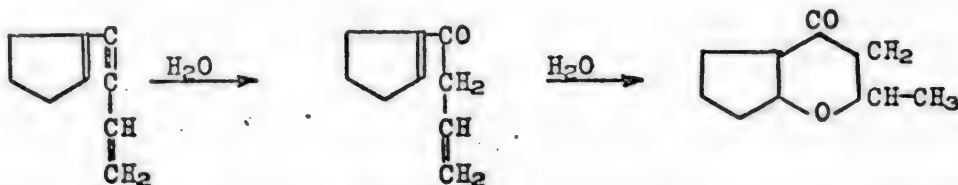
This peculiarity of the behavior of allyl-Δ¹-cyclopentenyl ketone is undoubtedly associated with the difficulty of formation of condensed five-membered ring systems due to steric hindrance. In this connection it appeared of interest to investigate the cyclizing ability of other allyl-Δ¹-cyclopentenyl ketones and, in particular, to study the influence of substituents in the cyclopentenyl molecules on the cyclization reaction. The starting material for the projected syntheses was the readily accessible 2,4-dimethylcyclopentan-1-one, condensation of

which with vinylacetylene in presence of pulverized potassium hydroxide yielded 2,4-dimethyl-1-vinylethynylcyclopentan-1-ol (I) in 74% yield. The latter is smoothly hydrogenated in alcoholic solution over platinum catalyst, taking up the theoretically required three molecules of hydrogen and being converted into 2,4-dimethyl-1-butylcyclopentan-1-ol (II). Just like other tertiary vinylethynyl carbinols, 2,4-dimethyl-1-vinylethynylcyclopentan-1-ol (I) is readily dehydrated on heating (60-65°) with sulfuric acid (50%), and gives 2,4-dimethyl-1-vinyleth-ynyl-Δ^2-cyclopentene (III) in 84% yield.

In presence of Pt catalyst the dienyne (III) in alcoholic solution adds on 4 molecules of hydrogen to form 2,4-dimethyl-1-butylcyclopentane (IV). When the dienyne (III) is heated in aqueous methanol solution in presence of mercuric sulfate it is readily hydrated with formation of allyl-2,4-dimethyl-Δ^1-cyclopent-enyl ketone (V), hydrogenation of which in glacial acetic acid solution in pres-ence of Pt catalyst is accompanied by addition of 2 molecules of hydrogen to form propyl-2,4-dimethylcyclopentyl ketone (VI) in about 70% yield. The struc-ture of the dienone (V) and in particular the position of the double bond in the ring were finally established by ozonation which led to formation of formic acid and the already known γ-acetylisovaleric acid (IX).
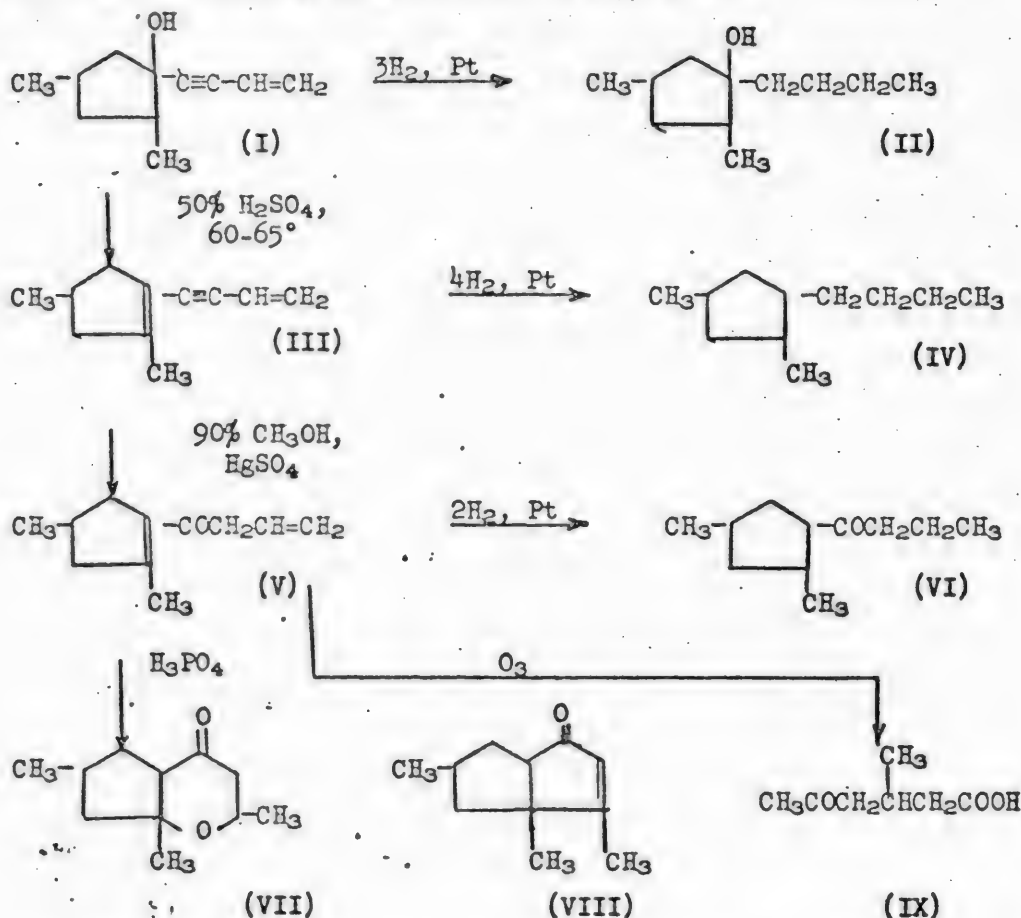
The latter readily forms the known semicarbazone and is oxidized by bromine-alkali with formation of bromoform. It was impossible, however, to isolate the β-methylglutaric acid owing to the serious contamination of the products of ox-idation with bromine-containing substances. Thus, the dehydration of the carbinol (I) proceeds only in a single direction with formation of a double bond in the ring on the side of the substituted carbon atom containing a methyl group. The

dehydration of the corresponding carbinols of the cyclohexane series also proceeds in a similar manner [3].

The dienone (V) is a cyclic analog of the substituted vinylallyl ketones which do not contain a free hydrogen in the vinyl radical. As demonstrated in a series of cases in our laboratory [4] these vinylallyl ketones are likewise very readily cyclized to cyclopentenones in presence of acid, but the double bond is in a different position:

$$R = CH_3, \ (CH_3)_2CH, \ (CH_3)_3C, \ C_6H_5.$$
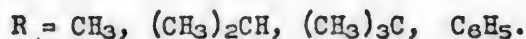
The application of such a cyclization procedure to vinylallyl ketones provides an easy route to polycyclic ketones containing the cyclopentanone ring with an angular methyl group, as was shown in respect of allyl-2-methyl-Δ^1-cyclohexenyl ketone [3].

In a series of cases these cyclizations proceed even more readily than the cyclization of the corresponding vinylallyl ketones possessing a free terminal hydrogen on the vinyl radical.

In conformity with the above scheme, the cyclization of the dienone (V) should be accompanied by the formation of trimethylbicyclooctenone (VIII). Like allyl-Δ^1-cyclopentenyl ketone, however, the dienone (V) is completely incapable of cyclization, and in presence of dilute phosphoric acid (sp. gr. 1.55) it undergoes hydration only to the bicyclic pyrone (VII). With more concentrated phosphoric acid (sp. gr. 1.7-1.8) the dienone (V) suffers marked resinification. Thus, the behavior of the dienone (V) again confirms the inability of substituted vinylallyl ketones to undergo cyclization when the vinyl group enters into a five-membered ring.

It was also impossible to prepare trimethylbicyclooctenone (VIII) by direct cyclohydration of the dienyne (III) with the aid of phosphoric acid, although by heating vinyl-Δ^1-cyclopentenylacetylene with phosphoric acid, as previously demonstrated [2], it is possible to effect cyclohydration and to isolate 1-methyl-(0,3,3)-bicyclo-$\Delta^{7,8}$-octen-3-one in a yield of approximately 30%:
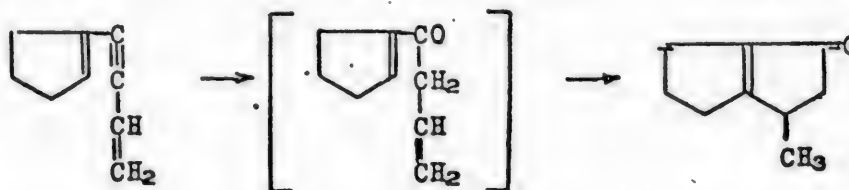
On the basis of the extensive experimental material on the cyclization of substituted vinylallyl ketones to cyclopentenones, we can state a general rule for the limitations of this interesting reaction, to the effect that all substituted vinylallyl ketones in which the vinyl group enters into a five-membered

ring system are incapable of undergoing cyclization to cyclopentenones but in-
stead undergo hydration to the corresponding tetrahydro-γ-pyrones. The inability
of allyl-Δ^1-cyclopentenyl ketones to undergo cyclization is entirely due to the
presence of the cyclopentene ring and clearly demonstrates the exceptional dif-
ficulty of forming polycyclic systems consisting of condensed five-membered
rings.   In all probability this is also the explanation of the difficult acces-
sibility of this class of products and of their complete absence in nature.

EXPERIMENTAL

The starting material, 2,4-dimethylcyclopentan-1-one (b.p. 152-154°;
n_D^{20} 1.4312) was prepared by hydrogenation of 2,4-dimethyl-Δ^2-cyclopenten-1-one,
which is readily obtained by hydration of vinylisopropenylacetylene and subse-
quent cyclization of the resultant allylisopropenyl ketone [5].

Synthesis of 2,4-dimethyl-1-vinylethynylcyclopentan-1-ol

In a three-necked round-bottomed flask equipped with mechanical stirrer,
thermometer, and dropping funnel were placed 80 g of potassium hydroxide powder
and 250 ml of dry ether, and addition was made of 25 g of vinylacetylene while
cooling with ice and salt (-5°). While constantly stirring and cooling (-5°),
a mixture of 100 g of 2,4-dimethylcyclopentan-1-ol, 100 ml of ether, and 60 g of
vinylacetylene was then introduced through the dropping funnel in the course of
an hour. The reaction mass was then stirred for 4 hours at -5°, and for 3 hours
at room temperature. On the following day the alkali was carefully removed with
water (100 ml), the product extracted with ether, washed with 5% hydrochloric
acid until the alkali was completely removed, dried with potassium carbonate,
and fractionated in vacuum, yielding 100 g of 2,4-dimethyl-1-vinylethynylcyclo-
pentan-1-ol (I) in the form of a viscous, colorless, transparent liquid:

B.p. 74-75° at 3 mm, n_D^{20} 1.4966; d_4^{20} 0.9344; MR found 50.20, computed
49.80.

3.580 mg substance: 3.863 mg CO_2; 3.081 mg H_2O.
Found %: C 80.27; H 9.64.
$C_{11}H_{16}O$. Computed %: C 80.43; H 9.83.

Hydrogenation of 2,4-dimethyl-1-vinylethynylcyclopentan-1-ol

4 g of the substance in 20 ml ethyl alcohol was hydrogenated in the pres-
ence of Pt catalyst for 1.5 hours when 1,670 ml of hydrogen (3 molecules) were
taken up. Fractionation of the product in vacuum yielded 2.9 g of 2,4-dimethyl-
-1-butylcyclopentan-1-ol (II) in the form of a viscous, colorless and trans-
parent liquid:

B.p. 91-92° at 10 mm, n_D^{20} 1.4560; d_4^{20} 0.8853; MR found 52.24, com-
puted 52.32.

7.570 mg substance. 21.507 mg CO_2; 8.808 mg H_2O.
3.360 mg substance: 9.558 mg CO_2; 3.845 mg H_2O.
Found %: C 77.54, 77.50; H 13.00, 12.76.
$C_{11}H_{22}O$. Computed %: C 77.57;   H 13.03.

Dehydration of 2,4-dimethyl-1-vinylethynylcyclopentan-1-ol

A mixture of 100 g of 2,4-dimethyl-1-vinylethynylcyclopentan-1-ol and 100
ml of 50% sulfuric acid, together with a small quantity of pyrogallol, was mixed
for 4 hours at 60-65°. On cooling, the layer of hydrocarbon was separated; the
aqueous layer was then extracted with ether, the product washed with soda solu-
tion, dried with sodium sulfate, and distilled in vacuum. There was obtained 75
g of 2,4-dimethyl-1-vinylethynyl-Δ^1-cyclopentene (III) in the form of a mobile,
light yellow transparent liquid:

B.p. 78-80° at 10 mm; n_D^{20} 1.5240; d_4^{20} 0.8705; MR found 51.35; computed 47.80.

3.190 mg substance: 10.533 mg CO_2; 2.338 mg H_2O.
Found %: C 90.08; H 9.95.
$C_{11}H_{14}$. Computed %: C 90.30; H 9.70.

Hydrogenation of 2,4-dimethyl-1-vinylethynyl-Δ^1-cyclopentene

4.5 g substance in 20 ml of methyl alcohol was hydrogenated over Pt catalyst. Hydrogenation was complete in 12 hours with absorption of 2,900 ml of hydrogen (4 molecules). Fractionation of the hydrogenation product in vacuum yielded 3 g of 2,4-dimethyl-1-butylcyclopentane (IV) in the form of a mobile, colorless, transparent liquid:

B.p. 58-58.5° at 8 mm; n_D^{20} 1.4380; d_4^{20} 0.8008; MR found 50.54, computed 50.80.

3.370 mg substance: 10.580 mg CO_2; 4.300 mg H_2O.
3.025 mg substance: 9.500 mg CO_2; 3.863 mg H_2O.
Found %: C 85.66, 85.71; H 14.28, 14.28.
$C_{11}H_{22}$. Computed %: C 85.62; H 14.38.

Hydration of 2,4-dimethyl-1-vinylethynyl-Δ^1-cyclopentene

a) A mixture of 105 g of 90% methyl alcohol, 2 g of mercuric sulfate and 35 g of dienyne (III) was agitated at 65° for 45 minutes. The methyl alcohol was distilled off in a low vacuum on the water bath (50°), and the residue extracted with ether. The ether extract was neutralized with soda solution, dried with sodium sulfate, and fractionated in vacuum to give 26.5 g of 1-allyl-2,4-dimethyl-Δ^1-cyclopentenyl ketone (V) in the form of a mobile, yellow, transparent liquid.

B.p. 94-94.5° at 4 mm; n_D^{20} 1.5020; d_4^{20} 0.9397; MR found 51.54; computed 49.87.

6.75 mg substance: 19.95 mg CO_2; 6.01 mg H_2O.
6.63 mg substance: 19.59 mg CO_2; 6.01 mg H_2O.
Found %: C 80.66, 80.64; H 9.96, 10.14.
$C_{11}H_{16}O$. Computed %: C 80.43; H 9.83.

b) 4.25 g of 90% methyl alcohol, 2.6 g of mercuric sulfate, and 140 g of dienyne (III) were agitated at 64° for 40 minutes. The methyl alcohol was distilled off in a low vacuum on the water bath (50°) for one hour, the residue extracted with ether, and the ether extract neutralized with soda solution, dried with sodium sulfate and fractionated in vacuum. There was obtained 149 g of a mixture of the dienone (V) and the corresponding methoxy ketone (β-methoxypropyl- -2,4-dimethylcyclopentenyl ketone) in the form of a mobile, yellow liquid boiling at 77-96° at 3 mm; n_D^{20} 1.4875-1.4808. This mixture was heated for 20 minutes in a 100 mm vacuum at 130-135°, in the presence of 0.15 g of p-toluenesulfonic acid, when 15 g of methyl alcohol came over. Distillation of the residue in vacuum yielded 115 g of allyl-2,4-dimethyl-Δ^1-cyclopentenyl ketone (V), b.p. 82-83.5° at 2.5 mm, n_D^{20} 1.5020.

Hydrogenation of allyl-2,4-dimethyl-Δ^1-cyclopentenyl ketone

3 g of substance in 10 ml glacial acetic acid was hydrogenated in presence of Pt catalyst. Hydrogenation was complete after 2.5 hours with absorption of 820 ml hydrogen (2 molecules). The product was neutralized with caustic alkali, extracted with ether, and the ether extract dried with sodium sulfate and fractionated to yield 2 g of propyl-2,4-dimethylcyclopentenyl ketone (VI) in the form of a mobile, colorless liquid.

B.p. 202-204°; n_D^{20} 1.4450; d_4^{20} 0.8757; MR found 51.10, computed 50.81.

Ozonation

Ozonized oxygen was passed for 19 hours at a rate of 4.5 liters/hour (ozone concentration 5%) through a solution of 8 g of the substance in 35 ml of dry chloroform. After the ozonization, the chloroform solution of the ozonide was poured into 30 ml of water, and the mixture stirred for 3 hours at room temperature. On the following day 6 ml of 30% hydrogen peroxide was added and the mixture again agitated at 50-60° for 6 hours. The product was neutralized with soda (9 g), the chloroform layer separated, and the aqueous layer extracted with ether. After distilling off the ether and chloroform on the water bath, 1.2 g of neutral products were obtained in the form of a transparent yellow oil which was not further examined.

Using the calomel method, the aqueous solution of salts was found to contain 1.28 g of formic acid (58% of theory). The solution of salts was evaporated to dryness in vacuum, the residue treated with concentrated hydrochloric acid (20 ml), and extracted with ether. The ether extract of the organic acids was dried with sodium sulfate and fractionated, yielding 1 g formic acid with b.p. 98-101.5° at 750 mm and 2.8 g of γ-acetylisovaleric acid (IX) with b.p. 120-128° at 2.5 mm and n_D^{20} 1.4460: In agreement with the literature, the semicarbazone of this keto acid melted at 171-172° [8] (from methanol).

Oxidation of γ-acetylisovaleric acid with bromine-alkali gave bromoform and a dark, uncrystallizable oil apparently comprising a mixture of the products of its oxidation and partial bromination.

Hydration of allyl-2,4-dimethyl-Δ^1-cyclopentenyl ketone to the bicyclic pyrone (VII)

a) A mixture of 115 g dienone (V) and 115 ml of phosphoric acid (sp. gr. 1.55) was agitated for 22 hours at room temperature. The product was dissolved in ether, neutralized with soda solution, dried with sodium sulfate, and fractionated in vacuum to yield 100 g of a mixture of the original material (V) and bicyclic tetrahydro-γ-pyrone (VII). Fractionation of this mixture in a vacuum column of 10 theoretical plates gave 12.5 g of the initial dienone (b.p. 85-86.5° at 3 mm, n_D^{20} 1.5030) and 45 g of the bicyclic pyrone (VII) in the form of a mobile, colorless liquid:

B.p. 92.5-93° at 8 mm; n_D^{20} 1.4682; d_4^{20} 0.9927; MR found 51.02, computed 50.25.

The semicarbazone of the bicyclic pyrone (VII) melted at 168-168.5° (from methyl alcohol).

b) A mixture of 12.5 g of dienone (V), 25 ml of 10% sulfuric acid, 45 ml of acetone, and 2 g of mercuric sulfate [7] (introduced in uniform portions throughout the whole period of the experiment) was agitated at 65° for 24 hours. When the heating was completed, the mixture was saturated with potassium carbonate and extracted with ether. The ether extract was dried with sodium sulfate and fractionated to yield 5.5 g of pyrone (VII) in the form of a colorless mobile liquid, b.p. 78-82° at 3.5 mm, n_D^{20} 1.4715. The semicarbazone melted at 167.5-168° and did not depress the m.p. of the semicarbazone of the pyrone from the preceding experiment.

On shaking a solution of the pyrone (VII) in glacial acetic acid in a hydrogen atmosphere in presence of Pt catalyst, no absorption of hydrogen was detected and the substance was recovered unchanged.

Numerous attempts to cyclize the dienone (V) in the presence of phosphoric acid or to effect direct cyclohydration of the dienyne (III) to trimethyl-bicyclooctenone (VIII) ended in failure. The compound resinified considerably when heated with concentrated phosphoric acid (sp. gr. 1.7-1.8), while treatment with dilute phosphoric acid only led to separation of the starting products and the bicyclic pyrone (VII).

SUMMARY

1. Condensation of 2,4-dimethylcyclopentan-1-ol with vinylacetylene in presence of pulverized potassium hydroxide gave 2,4-dimethyl-1-vinylethynylcyclopentan-1-ol in 74% yield, and dehydration of the latter by heating with 50% sulfuric acid resulted in the formation of 2,4-dimethyl-1-vinylethynyl-Δ^1-cyclopentene (III) in 84% yield.

2. 2,4-Dimethyl-1-vinylethynyl-Δ^1-cyclopentene (III) smoothly undergoes hydration in a medium of aqueous methyl alcohol in presence of mercuric sulfate, forming allyl-2,4-dimethyl-Δ^1-cyclopentenyl ketone (V) in 68% yield.

3. In contrast to other substituted vinylallyl ketones, allyl-2,4-dimethyl--Δ^1-cyclopentenyl ketone (V), like the previously investigated allyl-Δ^1-cyclopentenyl ketone, proved to be completely incapable of cyclization to the corresponding cyclopentenone [trimethyl-bicyclooctenone (VIII)], and under the influence of phosphoric acid it only hydrates to bicyclic tetrahydro-γ-pyrone (VII).

4. The demonstrated inability of allyl-Δ^1-cyclopentenyl ketones to undergo cyclization to the corresponding bicyclooctenones is the consequence of steric hindrance and testifies to the difficulty of formation of polycyclic systems with condensed five-membered rings and to their special stereochemical structure.

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INTRAMOLECULAR REARRANGEMENTS IN THE ACETYLENE SERIES

VI. PREPARATION OF METHYL-TERT-BUTYLMETHYLETHYNYLCARBINOL

AND ITS REACTIONS WITH HYDROGEN CHLORIDE

REACTION OF 2,2,3-TRIMETHYL-3-CHLOROHEXYNE-4 WITH SILVER ACETATE

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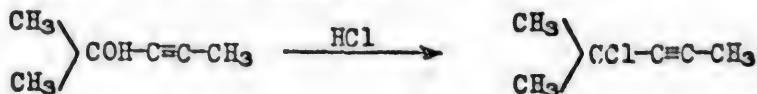
Tertiary acetylenic alcohols are now readily accessible thanks to the well-known reaction of A.E.Favorsky — the condensation of acetylene or its derivatives with ketones in presence of pulverized potassium hydroxide [1-3]. This reaction was later applied to the synthesis of tertiary vinylethynyl alcohols [4], acetylenic glycols [5-7], tribasic acetylenic alcohols [a], and erythritols of the acetylenic series [a]. Recently the reaction has been extensively used by I.N. Nazarov for the preparation of acetylenic alcohols serving as starting materials for the synthesis of polycyclic compounds related to the sterols [9], as well as for the synthesis of complex heterocyclic compounds [10].
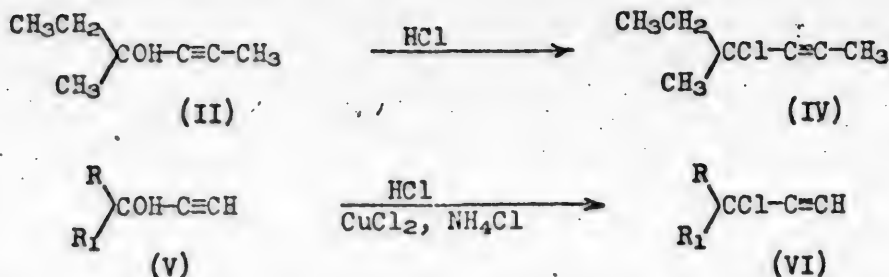
Some years ago the Favorsky reaction was first used by one of us for the synthesis of tertiary alcohols from acetylene and ketones. Condensation of propyne with acetone and methylethyl ketone yielded dimethylmethylethynyl and methylethylmethylethynyl carbinols (I and II) [11,12].

Attention was drawn at that time to some interesting properties of these alcohols.. Thus, the remarkable ease of substitution of the hydroxyl group by halogen was noted. The corresponding chlorides (III and IV) are obtained in very good yields by reacting the carbinols (I and II) with gaseous hydrogen chloride, but passage by the same route to chlorides of acetylenic tertiary alcohols of the type of (V) containing an unsubstituted acetylenic hydrogen is either impossible or only takes place to a very slight extent [11,14]. This method cannot be recommended for preparation of chlorides of the type of (VI). In most cases the latter are readily obtained and in good yields by Favorsky's method — the action on alcohols of concentrated hydrochloric acid in the presence of $CuCl_2$ and NH_4Cl [15].

Attention was also previously drawn to the difference in the behavior of chlorides of types (III) and (VI) with acetates, which will be discussed below.

As is evident from the examples given, previous work had shown that the substitution of the free acetylenic hydrogen in compounds of type (V) by the methyl group is clearly reflected in the properties both of the alcohols obtained in this manner and of their derivatives. It was of interest to confirm the previous observations by means of other examples.

$$\begin{matrix} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{matrix} COH-C{\equiv}C-CH_3 \xrightarrow{HCl} \begin{matrix} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{matrix} CCl-C{\equiv}C-CH_3$$

$$CH_3CH_2-\underset{\underset{CH_3}{|}}{C}OH-C\equiv C-CH_3 \quad (II) \xrightarrow{HCl} \quad CH_3CH_2-\underset{\underset{CH_3}{|}}{C}Cl-C\equiv C-CH_3 \quad (IV)$$

$$\underset{\underset{R_1}{|}}{\overset{\overset{R}{|}}{C}}OH-C\equiv CH \quad (V) \xrightarrow[CuCl_2, NH_4Cl]{HCl} \quad \underset{\underset{R_1}{|}}{\overset{\overset{R}{|}}{C}}Cl-C\equiv CH \quad (VI)$$

1. With this objective in view, the preparation is described here of the tertiary acetylenic alcohol, methyl-tert.-butylmethylethynyl carbinol (2,2,3-trimethylhexyn-4-ol-3 (VII), by Favorsky's reaction, from methylacetylene and pinacoline. Its properties are also investigated. An attempt was made to establish whether the substitution of the hydroxyl group in this alcohol by halogen would proceed readily, and the properties of the resultant chloride were studied.

It was found that the carbinol (VII), in a similar manner to the simplest members of this alcoholic series (I) and (II), is readily converted in 87% yield into the corresponding chloride, 2,2,3-trimethyl-3-chlorohexyne-4 (VIII), by treatment with gaseous hydrogen chloride. A study of the properties of the chloride (VIII) and the demonstration of its structure showed it to be a product of normal substitution of the hydroxyl group of carbinol (VII) by halogen.

$$(CH_3)_3C-\underset{\underset{CH_3}{|}}{C}OH-C\equiv C-CH_3 \xrightarrow{HCl} (CH_3)_3C-\underset{\underset{CH_3}{|}}{C}Cl-C\equiv C-CH_3$$
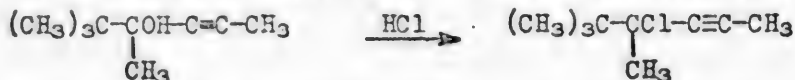
The chloride (VIII) readily hydrolyzes; on shaking with an aqueous solution of silver nitrate it rapidly yields a precipitate of AgCl, indicating that the chlorine is attached to the tertiary carbon atom and not at the double bond as would have been the case if the reaction had been accompanied by an acetylenic allenic rearrangement, which takes place during reaction of alcohols of type (VI) with concentrated HCl in presence of cuprous and cupric chloride [15].
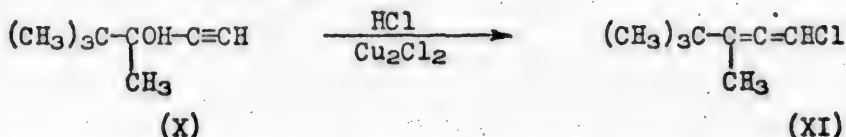
Theoretically, the substitution of a hydroxyl group of an alcohol containing a tertiary butyl radical could be accompanied by rearrangement with a change in the fundamental skeleton of the molecule, such as was reported, for.instance, by Favorsky and Sakar [16] in respect of the action of hydrogen bromide on tert.-amylcarbinol. In such a case the possibility might arise of formation of the chloride (IX) in addition to chloride (VIII) due to translocation of the methyl group.

$$CH_3-\underset{\underset{CH_3}{|}}{C}Cl-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-C\equiv C-CH_3 \quad (IX)$$
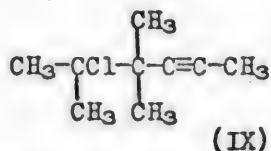
In our case, the action of hydrogen chloride upon methyl-tert.-butylmethylethynyl carbinol (VII) is not accompanied by any change in the skeleton of the molecule of the alcohol, as was demonstrated by oxidation of the resultant chloride with alkaline permanganate. The oxidation products detected were pinacoline and acetic acid, thus indicating structure (VIII) for the chloride. It should be mentioned that the chloride could not be oxidized in the cold. It was oxidized by a 1% alkaline solution of permanganate on heating on the water bath to 50°. It was not possible to establish the identity of the initial products of oxidation - methyl-tert.-butyl chloracetic acid or methyl-tert.-butyl hydroxyacetic acid. Under the reaction conditions they apparently undergo further oxidation to pinacoline.

It is interesting to compare the data obtained by us for the action of

gaseous hydrogen chloride on methyl-tert.-butylmethylethynyl carbinol (VII) with the results of I.A.Favorsky's study of methyl-tert.-butylethynyl carbinol (X), synthesized by the Favorsky reaction from acetylene and pinacoline. As is evident from a comparison of the structural formulas of these two carbinols, the alcohol (X) contains a free acetylenic hydrogen, while in alcohol (VII) this hydrogen is replaced by a methyl group. I.A.Favorsky found that conversion of carbinol (X) into the chloride could only be effected by prolonged action of hydrochloric acid in the presence of cuprous chloride. The resultant chloride did not possess the structure of the original alcohol but was a product of the acetylenic-allenic rearrangement (XI).

$$(CH_3)_3C-\underset{\underset{CH_3}{|}}{C}OH-C\equiv CH \quad \xrightarrow{\dfrac{HCl}{Cu_2Cl_2}} \quad (CH_3)_3C-\underset{\underset{CH_3}{|}}{C}=C=CHCl$$

$$\text{(X)} \qquad\qquad\qquad\qquad\qquad \text{(XI)}$$

In discussing the results obtained, Favorsky draws attention to the marked difference between the reaction of hydrogen chloride with saturated tertiary alcohols containing a tert.-butyl radical and the reaction of methyl-tert.-butylethynyl carbinol (X) with hydrochloric acid. The carbinol (X) could not be converted into the corresponding chloride, although the saturated tertiary alcohol, diethyl-tert.-butyl carbinol, reacts instantaneously with hydrogen chloride, according to the literature [17]. Whereas saturated tertiary alcohols readily form a carbonium ion and enter into a monomolecular reaction with hydrogen chloride, tertiary alcohols of type (V) eveidently undergo a bimolecular reaction with HCl. The presence in these alcohols of the acetylenic radical results in a fall in the electronic density at the central carbon atom, hinders the formation of carbonium ion, and thereby hinders the monomolecular course of the reaction. From this standpoint we can understand why, as noted by I.A.Favorsky, the methyl-tert.-butylethynyl carbinol (X) is exceptionally resistant to substitution by halogen of the hydroxyl group. The velocity of bimolecular substitution in this alcohol is reduced by the steric hindrance arising from the presence of the neopentyl group; in other words, the inertness of methyl-tert.-butylethynyl carbinol (X) during bimolecular substitution is due to steric and not to polar factors, and the substitution proceeds entirely with molecular rearrangement.

Coming now to a consideration of the results described in the present paper on the reaction of gaseous hydrogen chloride with methyl-tert.-butylmethylethynyl carbinol (VII), it should be noted that a particularly clear demonstration was given of the marked influence of the presence of a methyl group in place of a free acetylenic hydrogen on the course of the reaction of substitution of a hydroxyl group by halogen in tertiary acetylenic alcohols. Both of the carbinols (VII) and (X) contain the neopentyl group,

$$(CH_3)_3C-C\overset{\diagup}{-},$$
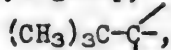
which in alcohol (X) is linked to the -C≡CH residue, and in alcohol (VII) to the -C≡C-CH3 residue. In their behavior towards hydrogen chloride these two carbinols are entirely different. Whereas according to the data of I.A.Favorsky [14], methyl-tert.-butylethynyl carbinol (X) generally failed to undergo transformation into the corresponding chloride, in the case of methyl-tert.-butylmethylethynyl carbinol this transformation proceeds, as shown by our results, with unusual ease, and the resultant chloride has a structure corresponding to that of the original alcohol. Furthermore, the chlorine in chloride (VIII) is so mobile that it is quantitatively precipitated by silver nitrate.

The foregoing facts justify the conclusion that the mechanism of substitution

The simplest tertiary acetylenic alcohols of type (V), as already pointed out, are readily transformed into the corresponding chlorides only by treatment with conc. hydrochloric acid in presence of CuCl2.

of the hydroxyl group by halogen in alcohol (VII) differs from that in alcohol (X). Whereas in the case of monosubstituted acetylenic alcohols the presence of an acetylenic residue diminishes the electron density at the central carbon atom, obstructs the formation of the carbonium ion, and thereby facilitates a bimolecular course of the substitution reaction, the replacement of the free acetylenic hydrogen by the methyl group produces the opposite effect. The positive inductive effect of the methyl group, reinforced by the effect of hyperconjugation of the C-H bonds of the methyl group with a triple bond, increases the electron density at the central carbon atom, increases the mobility of the hydroxyl group in alcohols (I, II, VII) and the mobility of the chlorine in chlorides (III, IV, VIII), facilitates the formation of carbonium ion, and makes possible a bimolecular mechanism for the course of the reaction of substitution of the hydroxyl group by halogen.

Even in the absence of kinetic data, the very fact of the greater reactivity of methyl-tert.-butylmethylethynyl carbinol (VII) in comparison with methyl-tert.-butylethynyl carbinol (X) justifies the a priori conclusion that the reaction of carbinol (VII) with hydrogen chloride proceeds according to a monomolecular mechanism.
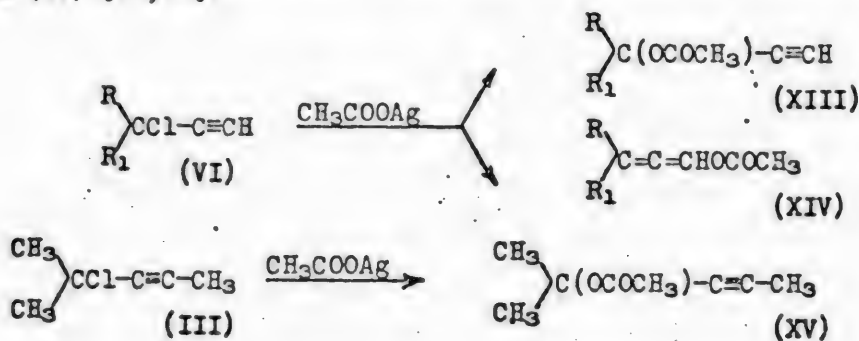
On the basis of the results obtained in the present investigation and in our previous study of the reaction of gaseous hydrogen chloride with carbinols of the same series (I and II) [11,12], analogous conclusions may be drawn about the mechanism of these reactions, since the conditions in all of the three cases were perfectly identical and no differences were observed in the course of the reactions.

Consequently, the replacement of one of the radicals at the central carbon atom of tertiary acetylenic alcohols of the type of (XII)
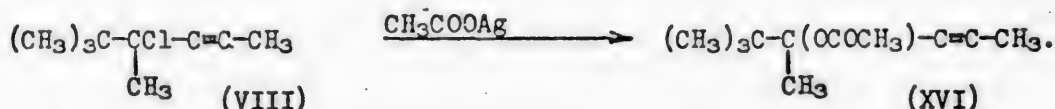
$$\begin{array}{c} R \\ R_1 \end{array}\!\!\!\!\!\!\rangle COH-C\equiv C-CH_3$$

(XII)
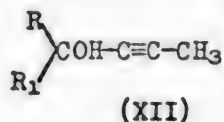
by the tert.-butyl group provided an indirect method — avoiding kinetic experiments — of drawing perfectly precise conclusions about the mechanism of the substitution of the hydroxyl group of alcohols of this series by halogen.

2. The next stage in the investigation was the study of the reaction of the chloride, 2,2,3-trimethyl-3-chlorohexyne-4 (VIII), with silver acetate in a glacial acetic acid medium. One of us had previously shown [18] that the reaction of a chloride of the type of (VI) with silver acetate under the specified conditions is accompanied by intramolecular rearrangement, resulting in the formation, side by side with the acetate of the normal acetylenic structure (XIII) of an acetate with the allenic structure (XIV). However, the reaction between silver acetate and chlorides (III) and (IV) yielded only products of normal substitution (XV) [11,12].

$$\begin{array}{c} R \\ R_1 \end{array}\!\!\!\!\!\!\rangle CCl-C\equiv CH \quad \xrightarrow{CH_3COOAg}$$

(VI)

$$\begin{array}{c} R \\ R_1 \end{array}\!\!\!\!\!\!\rangle C(OCOCH_3)-C\equiv CH$$

(XIII)

$$\begin{array}{c} R \\ R_1 \end{array}\!\!\!\!\!\!\rangle C=C=CHOCOCH_3$$

(XIV)

$$\begin{array}{c} CH_3 \\ CH_3 \end{array}\!\!\!\!\!\!\rangle CCl-C\equiv C-CH_3 \quad \xrightarrow{CH_3COOAg}$$

(III)

$$\begin{array}{c} CH_3 \\ CH_3 \end{array}\!\!\!\!\!\!\rangle C(OCOCH_3)-C\equiv C-CH_3$$

(XV)

A completely analogous course of reaction has now been observed in the case of the chloride, 2,2,3-trimethyl-3-chlorohexyne-4 (VIII), when treated with silver acetate under the conditions used for chlorides (III) and (IV) [11,12]. Only one acetate was obtained, and to this must be ascribed the structure of the acetylenic derivative (XVI) on the basis of a study of its properties.

The same acetate was obtained by another route, by the action of acetic anhydride on carbinol (VII). A comparison revealed the complete identity between the constants of the acetate obtained from chloride (VIII) by reaction with CH_3COOAg and that prepared directly from carbinol (VII) by treatment with acetic anhydride:

$$(CH_3)_3C-CCl-C\equiv C-CH_3 \quad \xrightarrow{CH_3COOAg} \quad (CH_3)_3C-C(OCOCH_3)-C\equiv C-CH_3.$$
$$\underset{\displaystyle CH_3 \quad (VIII)}{} \qquad\qquad\qquad \underset{\displaystyle CH_3 \qquad (XVI)}{}$$

Certain features thus characterize the reactions of tertiary acetylenic chlorides with silver acetate in a glacial acetic acid medium.

The halogen atoms in chlorides (III, IV, and VIII), as already noted above, are more mobile and therefore more reactive than those in chlorides of the type of (VI) with an unsubstituted acetylenic residue owing to their specific relationship to the terminal methyl group through the tertiary bond. Thus, an intramolecular rearrangement during substitution of halogen in the acetic acid residue can only take place in the case of chlorides of the type of (VI), while those of the type of (III), (IV), or (VIII) on reaction with CH_3COOAg only yield products of normal substitution – acetylenic acetates.

It should be taken into consideration that our previous studies [12,18] had likewise shown that allenic acetates are unstable and under the conditions of reaction they isomerize to acetylenic derivatives:

$$\underset{\displaystyle R_1 \quad (XIV)}{\overset{\displaystyle R}{>}}C=C=CHOCOCH_3 \quad \longrightarrow \quad \underset{\displaystyle R_1 \qquad (XIII)}{\overset{\displaystyle R}{>}}C(OCOCH_3)-C\equiv CH.$$

Formation of the allenic acetate (XIV) could only be observed when the process was not unduly prolonged and when a certain temperature was strictly maintained.

In the above connection it may be suggested that intramolecular rearrangement also takes place during the reactions of chlorides (III), (IV), and (VIII) with silver acetate to give an acetate of anomalous allenic structure of the type of (XVII):

$$\underset{\displaystyle R_1}{\overset{\displaystyle R}{>}}C=C=C\underset{\displaystyle CH_3}{\overset{\displaystyle OCOCH_3}{}}$$
$$(XVII)$$
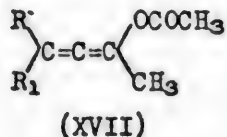
Such a compound, however, is unstable, and under the reaction conditions it readily changes into the normal acetylenic acetate. Unfortunately, the results of our research do not provide any concrete data to enable us to decide whether an acetate of the type of (XVII) is formed, or whether it is capable of existence; nor can we express any opinion as to the ease of its transformation into the acetylenic acetate.

In view of the complexity of the processes under consideration, the problem of their mechanism remains unsolved and calls for further research.

<div align="center">EXPERIMENTAL</div>

1. Preparation of methyl-tert.-butylmethylethynyl carbinol (VII) (2,2,3-trimethylhexyn-4-ol-3). The carbinol was synthesized according to A.E.Favorsky's

method. 200 g of pulverized potassium hydroxide and 400 ml of absolute ether
were introduced into a three-necked flask fitted with a rapidly rotating paddle
stirrer, a reflux condenser, and a dropping funnel. With rapid stirring and ex-
ternal cooling to 0°, a stream of methylacetylene was passed into the ether for
one hour. A solution of 110 g (1 mole) pinacoline in 100 ml ether was then added
dropwise over a period of 7 hours without interrupting the flow of methylacetyl-
ene and with continuance of the rapid stirring and the cooling. In all, about
25 liters of gas was introduced. After admission of the methylacetylene had
ceased, the stirring was continued for a further hour. The reaction mass was
left overnight and then treated with water while stirring and cooling. The ether
layer was separated from the alkaline solution, and the latter was subjected to
extraction with ether. The ether extracts were combined and dried with calcined
$MgSO_4$. The ether was distilled off and the residue fractionated in vacuum to
give two fractions, one boiling at 30-60° at 22 mm, and the other at 68-70° at
13 mm. A second fractionation of the first fraction yielded about 10 g of un-
changed pinacoline, and a second fractionation of the second fraction gave methyl-
tert.-butylmethylethynyl carbinol (X) in 65% yield:

B.p. 68° at 13 mm; d_4^0 0.8946; d_4^{20} 0.8767; n_D^{20} 1.45261; n_α^{20} 1.45006;
n_β^{20} 1.45881; MR_D 43.13; MR_α 42.93; MR_β 43.64.

$C_9H_{16}O$ ⊧. Computed: MR_D 43.22; MR_α 43.09; MR_β 43.87.

0.3698 g substance: 18.22 g benzene: Δt 0.75°.
0.2924 g substance: 16.95 g benzene Δt 0.64°.
Found: M 138.01, 137.47.
$C_9H_{16}O$. Computed: M 140.

0.1169 g substance: 0.3298 g CO_2; 0.1203 g H_2O.
0.1279 g substance: 0.3616 g CO_2; 0.1320 g H_2O.
Found %: C 76.94, 77.11; H 11.51, 11.54.
$C_9H_{16}O$. Computed %: C 77.14;   H 11.43.

This carbinol was first obtained by Iotsich and co-workers [13] by the action
of magnesium allene bromide on pinacoline. Iotsich reports the constants: b.p.
69° at 13 mm, d^{20} 0.8784.

2. Action of hydrogen chloride on methyl-tert-butylmethylethynyl carbinol.
Preparation of 2,2,3-trimethyl-3-chlorohexyne-- (VIII). 25 g carbinol was treated
with gaseous hydrogen chloride in portions of 4-5 g at a time. At the outset the
gas was completely absorbed; the temperature of the mixture was gradually in-
creased and at 70-75° a vigorous reaction took place; the mixture became turbid
but subsequently again became clear with separation into two layers, the upper
one of chloride and the lower one of water. The hydrogen chloride ceased to be
absorbed, indicating completion of the reaction. The chloride was washed seve-
ral times with cold soda, dried with calcium chloride, and distilled. Yield 50%
of theory:

B.p. 56-57° at 8 mm. m.p. 21°; d_4^{21} 0.9275; d_4^{25} 0.9251; n_D^{25} 1.46310;
n_1^{25} 1.46033; n_β^{25} 1.46994; MR_D 47.20; MR_α 47.04; MR_β 47.80.

$C_9H_{15}Cl$ ⊧. Computed: MR_D 46.62; MR_α 46.35; MR_β 47.21.

0.2440 g substance: 17.65 g benzene: Δt 0.455°.
0.3826 g substance; 17.80 g benzene: Δt 0.710°.
Found: M 154.95, 154.80.
$C_9H_{15}Cl$. Computed: M 158.50.

0.0981, 0.1685 g substance: 0.0859, 0.1493 g AgCl (Carius).
Found %: Cl 21.67, 21.94.
$C_9H_{15}Cl$. Computed %: Cl 22.40.

The percentage content of chlorine in the chloride is slightly below the theoretical amount, apparently due to contamination with a little of the original carbinol. It is interesting to note that almost identical results were obtained by direct precipitation with aqueous $AgNO_3$.

<div align="center">

0.1226 g substance: 0.1018 g AgCl.

Found %: Cl 20.55.

$C_9H_{15}Cl$. Computed %: Cl 22.40.

</div>

Oxidation of chloride (VIII). 6.25 g of chloride was oxidized with 1% alkaline $KMnO_4$ on the water bath at 50° while stirring. The neutral products of oxidation were distilled off in steam, giving an oily layer with the odor of pinacoline which was dried with $MgSO_4$ and then distilled into an acetic acid solution of semicarbazide. A precipitate was formed which after recrystallization from methyl alcohol melted at 155-156° and did not depress the melting point of an authentic specimen of pinacoline semicarbazone.

The solution remaining after removal of the neutral product was acidified with sulfuric acid and fractionated to give two 20 ml fractions. On heating with silver nitrate both of the fractions gave silver salts which analysis showed to be acetates.

<div align="center">

0.0324 g, 0.0862 g substance: 0.210, 0.0557 g Ag.

Found %: Ag 64.81, 64.61.

$C_2H_3O_2Ag$. Computed %: Ag 64.67.

</div>

Action of silver acetate on 2,2,3-trimethyl-3-chlorohexyne-4 (VIII). Preparation of 2,2,3-trimethyl-3-acetoxyhexyne-4 (XVI). 17 g of silver acetate (0.1 mole) and 20 ml glacial acetic acid were placed in a vessel fitted with a stirrer and coated with black paper to prevent decomposition of the silver salts. With vigorous stirring a solution of 16 g (0.1 mole) chloride in 10 ml of glacial acetic acid was run in dropwise over a period of 30 minutes. Heat was developed. The mixture was stirred for 4 hours at 60°. After conclusion of the heating, the mixture was diluted with water, the acid neutralized with 10% soda solution, and the reaction products extracted with ether. The ether solution was washed with 10% soda solution to neutralize the acid entrained with the ether, and then washed with water and dried with calcined sodium sulfate. The residue after removal of the ether was fractionated in vacuum, yielding the following fractions: 1) b.p. 29-45° at 10 mm (3 g); 2) b.p. 45-67° (2 g); 3) b.p. 67-70° at 7 mm (12 g). The third fraction, a colorless liquid with an ethereal odor, was again fractionated to give an acetate with b.p. 65° at 6 mm. Yield 11.5 g, or 63% of theory.

d_4^0 0.9321; d_4^{20} 0.9144; n_D^{20} 1.44316; n_α^{20} 1.44068; n_β^{20} 1.45128; MR$_D$ 52.77; MR$_\alpha$ 52.63; MR$_\beta$ 53.62.

$C_{11}H_{18}O_2$. Computed: MR$_D$ 52.53; MR$_\alpha$ 52.23; MR$_\beta$ 53.17.

<div align="center">

0.1608 g substance: 17.90 g benzene: Δt 0.255°.

0.1380 g substance: 17.50 g benzene: Δt 0.225°.

Found: M 179.16, 178.75.

$C_{11}H_{18}O_2$. Computed: M 182.

0.1026 g substance: 0.2707 g CO_2; 0.0904 g H_2O.

0.0835 g substance: 0.2199 g CO_2; 0.0741 g H_2O.

Found %: C 71.95, 71.82; H 9.85, 9.92.

$C_{11}H_{18}O_2$. Computed %: C 72.53; H 9.89.

</div>

Action of acetic anhydride on methyl-tert.-butylmethylethynyl carbinol (VII). A mixture of 8 g carbinol and 40 g acetic anhydride was heated on a sand bath for 6 hours, and then diluted with water, the upper ether layer separated, washed several times with water, dried with sodium sulfate, and distilled. The constants of

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Carried out by student R. A. Sapozhnikova.

the acetate obtained agreed with those for the acetate obtained by the action of silver acetate on chloride (VIII) in the preceding experiment:

B.p. 62-63° at 5 mm; d_4^0 0.9315; d_4^{20} 0.9138.

0.0881 g substance: 0.2354 g CO_2; 0.0877 g H_2O.
Found %: C 72.86; H 10.3.
$C_{11}H_{18}O_2$. Computed %: C 72.52; H 9.89.

SUMMARY

1. Methyl-tert.-butylmethylethynyl carbinol (VII) (2,2,3-trimethylhexyn-4-ol-3) was prepared by A.E.Favorsky's method from methylacetylene and pinacoline in presence of pulverized potassium hydroxide in ether.

2. The chloride, 2,2,3-trimethyl-3-chlorohexyne-4 (VIII), was obtained by reacting gaseous hydrogen chloride with the carbinol (VII), and its structure was established.

3. The substitution of the hydroxyl group by halogen in alcohol (VII) was found to follow a monomolecular mechanism.

4. The action of silver acetone on chloride (VIII) results in the formation of one acetate with an acetylenic structure (2,2,3-trimethyl-3-acetoxyhexyne-4) (XVI). Formation of the isomeric allenic acetate was not observed.

5. The acetate (XVI) was also prepared by the action of acetic anhydride on methyl-tert.-butylmethylethynyl carbinol (VII).

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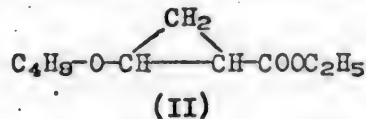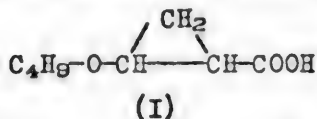[***] See CB translation p. 75 ff.

REACTIONS OF ALIPHATIC DIAZO COMPOUNDS WITH UNSATURATED COMPOUNDS

IV. HYDROLYSIS OF 1-BUTOXYCYCLOPROPANE-2-CARBOXYLIC ACID AND ITS ETHYL ESTER

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In previous communications [1,2,3] we described the preparation and properties of 1-butoxycyclopropane-2-carboxylic acid (I) and its ethyl ester (II):

$$C_4H_9-O-CH \overset{CH_2}{\diagup\diagdown} CH-COOH \qquad\qquad C_4H_9-O-CH \overset{CH_2}{\diagup\diagdown} CH-COOC_2H_5$$

$$\text{(I)} \qquad\qquad\qquad\qquad\qquad \text{(II)}$$

It was noted [3] that (I) is extremely unstable in an acid medium, partial hydrolysis being observed even on separation from salt solutions by the action of dilute sulfuric acid, when the $C_4H_9-O-CH\big\langle$ linkages are attacked. The products of hydrolysis were found to be butyl alcohol and a crystalline acid with the elementary composition $(C_8H_{10}O_5)_x$. The structure and mechanism of formation of this acid were not established at the time, since no special experiments on the hydrolysis of the cyclic acid (I) and its ester (II) had yet been carried out. At that time the hydrolytic fission of butoxycyclopropane carboxylic acid was merely a subsidiary reaction (and a most unwelcome one) during the preparation of the acid (I) itself. Even then, however, the suggestion was made that the hydrolysis of butoxycyclopropane carboxylic acid might be represented by the following scheme :

$$2C_4H_9O-CH \underset{CH_2}{\diagdown\diagup} CH-COOH + H_2O = 2C_4H_9OH + C_8H_{10}O_5.$$
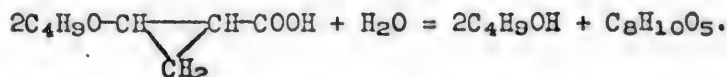
It is shown in the present investigation that the foregoing equation apparently possesses general significance both for the hydrolysis of acid (I) and of the ester (II):

$$2C_4H_9-O-CH \underset{CH_2}{\diagdown\diagup} CH-COOC_2H_5 + 3H_2O = 2C_4H_9OH + C_8H_{10}O_5 + 2C_2H_5OH.$$
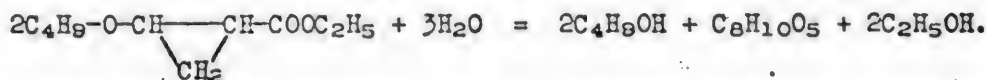
The same crystalline acid with m.p. 98-100° was also separated during the hydrolysis of the ester.

Data for the molecular weight of the acid of composition $(C_8H_{10}O_5)_x$ were not given in the previous communication and therefore the hydrolytic equation then advanced was to some extent hypothetical.

In the present paper it is shown that the equation may be correct because it has been found that the molecular weight of the acid $(C_8H_{10}O_5)_x$ is 186, i.e., the acid may be represented by the formula $C_8H_{10}O_5$.

However, the acid and ester differ in their stability to heating with sulfuric acid solutions. The acid is fully hydrolyzed even on boiling with 0.1 $\underline{N}$ sulfuric acid under conditions of good mechanical mixing (emulsification) of the reaction mixture, whereas under the same conditions the ester is only hydrolyzed in a 10% solution of sulfuric acid. However, this concentration of acid is not necessarily the minimum at which the ester undergoes fission, since it was observed (see 1,B, experimental) that slight hydrolysis also occurs on boiling the ester with 0.1 N sulfuric acid.

The ease of hydrolysis of the alkoxy group in butoxycyclopropane carboxylic acid and the sensitivity of the acid itself to oxidizing agents (see Communication III) are properties rather unusual in saturated ethers. More appropriate in this case is the analogy with the vinyl ethers, the instability and ease of oxidation of which (due to their unsaturation) are well known. On the basis of this analogy it may be suggested that ethers of cyclopropanol

$$\begin{array}{c} CH_2 \\ \diagup \quad \diagdown \\ CH_2 \!-\!\!-\!\!-\! CH\text{-}OR \end{array} \quad (R = alkyl)$$
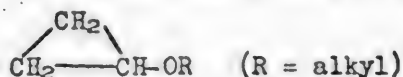
(which have been comparatively rarely described in the literature) will be similarly characterized by poor stability, readily oxidizing and readily hydrolyzing

at the $\overline{H}C\text{-}O\text{-}R$ bonds in presence of suitable reagents.[*]

The greater stability of the ethyl ester of butoxycyclopropane carboxylic acid in comparison with the acid itself is probably due to the stabilizing effect, long known in the literature, of the carbethoxy group on the carbon-carbon bonds of the trimethylene ring.

A summary of experiments on the hydrolysis of butoxycyclopropane carboxylic acid and its ester is given in Table 1. In both cases the yields of the crystalline acid $C_8H_{10}O_5$ range from 24 to 35% of theory; the yields set out in the table relate to the analytically pure preparation (m.p. 99-100°) or to a slightly impure product (m.p. 97-100°)[**]. The low yields of crystalline acid are caused by the loss during isolation and purification. Butyl alcohol was obtained in the hydrolysis reaction in 80% yield.

From the empirical analysis and the molecular weight determination, the formula $C_8H_{10}O_5$ may be ascribed to the acid. Later analytical determinations convinced us that the compound was an unsaturated dibasic aldehydo acid. The presence of two carboxyl groups was confirmed by determination of the neutralization equivalent of the acid and by determination of the percentage of silver in its silver salt. The aldehyde group was identified by the characteristic qualitative tests (silver mirror, Fehling solution reaction), as well as by the preparation of the semicarbazone which melted at 197-198° (after recrystallization from water)[***] and of the p-nitrophenylhydrazone, m.p. 198-199° (with decomp., recrystallized from alcohol). The analytical data for the semicarbazone agree with the the formula $C_9H_{13}O_5N_3$, which would be anticipated if one carbonyl group was present in the aldehydo acid. The analytical results demanded by theory could not be obtained for the p-nitrophenylhydrazone.

The double bond of the compound can be readily detected with the aid of

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[*] A further analogy between the alkylcyclopropyl ethers and the vinyl alcohol ethers resides in the fact that neither the simplest alcohol of the trimethylene series - cyclopropanol - nor the simplest unsaturated alcohol - vinyl alcohol - appears to be capable of existence.

[**] It should be noted that the yields of crude, uncrystallized product are much higher, in some experiments reaching 75% of theory.

[***] The unrecrystallized semicarbazone melts at 188-188.5°.

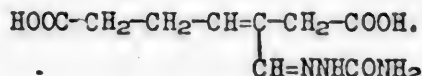bromine in chloroform solution, as well as by hydrogenation of the acid in presence of platinum black. In the latter reaction the amount of hydrogen adding on to an exactly weighed sample of the aldehydo acid was equivalent to that required for a single double bond [*].

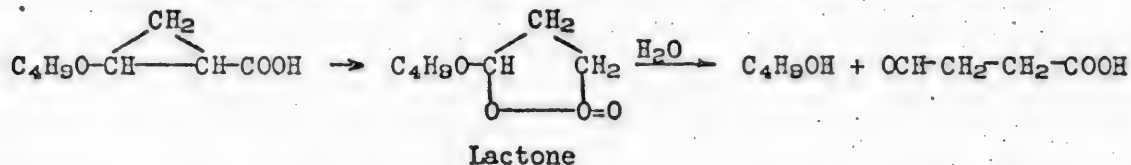On the basis of these data we propose formulas (III) and (IV) for the acid and its semicarbazone, respectively:
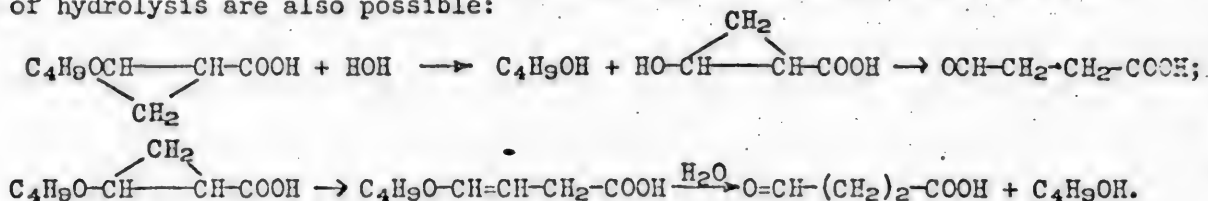
$$HOOC-CH_2-CH_2-CH=C-CH_2-COOH; \qquad HOOC-CH_2-CH_2-CH=C-CH_2-COOH.$$
$$\qquad\qquad\qquad CH=O \qquad\qquad\qquad\qquad\qquad\qquad CH=NNHCONH_2$$
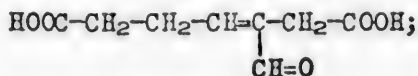
<div align="center">(III)   (IV)</div>

If these formulas are correct, we may regard the acid $C_8H_{10}O_5$ as the product of aldol condensation of two molecules of aldehydosuccinic acid. It has been repeatedly shown [3] that aldehydosuccinic acid is one of the possible final products (although not yet isolated by us) of hydrolysis of the cyclic acid:

$$C_4H_9O-CH---CH-COOH \rightarrow C_4H_9O-CH \quad CH_2 \xrightarrow{H_2O} C_4H_9OH + OCH-CH_2-CH_2-COOH$$

<div align="center">Lactone</div>

Other mechanisms of the formation of aldehydosuccinic acid during the process of hydrolysis are also possible:

$$C_4H_9OCH---CH-COOH + HOH \longrightarrow C_4H_9OH + HO-CH---CH-COOH \rightarrow OCH-CH_2-CH_2-COOH;$$

$$C_4H_9O-CH---CH-COOH \rightarrow C_4H_9O-CH=CH-CH_2-COOH \xrightarrow{H_2O} O=CH-(CH_2)_2-COOH + C_4H_9OH.$$

At the present time it is impossible to make a choice between these schemes. It is still impossible to say at which stage of the transformation and under which conditions the formation of the acid $C_8H_{10}O_5$ could take place. We can only make a few preliminary observations relevant to the problems here touched upon.

The acid $C_8H_{10}O_5$ is obtained as an oil on extraction with ether from aqueous solutions, and only after further treatment (sometimes by heating in vacuum) does it crystallize. It might therefore be thought that the oily product is aldehydosuccinic acid, which loses water (from two molecules of acid) on further treatment and is converted into crystals of the more complex acid $C_8H_{10}O_5$.

This theory must, however, be immediately rejected, since aldehydosuccinic acid, in contrast to the oily acid, is miscible with ether in all proportions; moreover, in some experiments we observed crystallization of the oil when the flask containing the extract was merely allowed to stand and without removal of the ether layer, i.e., under conditions hardly favorable to intermolecular condensation. Finally, the preparation of the p-nitrophenylhydrazone of the acid $C_8H_{10}O_5$ (m.p. 198°) from an aqueous solution of the products of hydrolysis before carrying out the ether extraction of this solution was clear evidence that the acid $C_8H_{10}O_5$ had already been formed in the aqueous solution.

In further work on the mechanism of formation of the acid $C_8H_{10}O_5$ we obtained

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[*] The carbonyl group in the $C_8H_{10}O_5$ acid under these conditions begins to hydrolize after the double bond has absorbed the theoretically required amount of hydrogen. Hydrogenation of the carbonyl group proceeds so slowly that we did not bring this reaction to a conclusion.

precise confirmation of the foregoing observations, details of which will be the subject of a separate communication. In the present paper we limit ourselves to consideration of work on the structure of the acid $C_8H_{10}O_5$ using the method of oxidation with permanganate in a neutral medium. The acid instantly decolorizes permanganate solution, and consumes more oxidizing agent than is required theoretically for complete oxidation of one double bond and one aldehyde group, (see experimental). We were unable to detect any neutral products of oxidation, such as would be expected on the basis of the above formula for the acid. The only dibasic acid that we were able to isolate was succinic acid, in approximately 60% yield. It was also shown that oxalic acid is not formed during the oxidation of this compound. We were unable to detect acetic acid in the products of oxidation, although a very small amount of the silver salt was obtained in one experiment (from an acid fraction boiling at 100-145° at 760 mm), and which analyzed to 62.13% Ag as against 64.66% Ag required for silver acetate. In the remaining experiments very small amounts of substances which were volatile in steam were formed (apparently lower acids), but we were unable to characterize these by conversion into silver salts owing to their instablity in aqueous solutions.

The formation of succinic acid during oxidation of the acid of composition $C_8H_{10}O_5$ is in good agreement with our above formula. The non-formation of any other oxidation products, apart from succinic acid during decomposition with permanganate, when the amount of permanganate consumed was much higher than the theoretical requirement, would seem to indicate that the complex acid residue comprising the right-hand portion of the formula here undergoes complete decomposition to lower oxidation stages which we did not isolate. An initial stage of the oxidation of this residue could be oxalacetic acid, which is known [5] to be very unstable and to decompose even in aqueous solution with formation of CO_2, H_2O, and pyroracemic acid. Under oxidizing conditions the latter in turn could yield acetic acid, although we were unable to obtain convincing evidence that this actually took place. Another possible mode of oxidation of the right-hand portion of the formula could involve the formation of oxalic acid, although here again we failed to obtain experimental evidence.

On carrying out the oxidation of the acid with a deficiency of permanganate (1 mole acid to 1 mole oxidizing agent), no definite results were obtained, although the formation of succinic acid was again observed. In the absence at present of any further data relating to the structure of the acid $C_8H_{10}O_5$, we are compelled to use the first of the above-proposed mechanisms of oxidation, while trusting that further work will reveal other facts in suport of the structure proposed.

EXPERIMENTAL

1. Action of Solutions of Sulfuric Acid on 1-Butoxycyclopropane 2-Carboxylic Acid and Its Ethyl Ester

A. Hydrolysis of 1-butoxycyclopropane-2-carboxylic acid and isolation of the acid $C_8H_{10}O_5$. 35 g of butoxycyclopropane-carboxylic acid (b.p. 134-136° at 8 mm) and 250 ml of 0.1 N sulfuric acid were heated to boiling with rapid stirring until the solution was completely transparent (a slight turbidity appeared on cooling but this did not affect the further operations). The cooled solution was then neutralized with caustic soda and distilled with steam. The butyl alcohol collected in the first fraction was separated from the water, dried, and distilled. B.p. 114-117°. Yield 13.5 g (82% of theory). After a second distillation the butyl alcohol had the constants: B.p. 116-117°, d_4^{20} 0.813; n_α^{20} 1.397. These are sufficiently close to the literature data.

The solution remaining in the distilling flask was concentrated to a volume of 150 ml and acidified with 80 ml 10% sulfuric acid. The acidified solution was

extracted with ether in a Soxhlet for 3 days. The resultant ether extract yielded a layer of yellow oil immiscible with ether. Since the individual experiments had shown that a small quantity of the product was nevertheless soluble in ether, the latter was driven off in vacuum. Gentle heating of the reaction product in vacuum also eliminates moisture. On cooling, the oil crystallized.

Some of the experiments for crystallization of the oil necessitated heating in vacuum on the boiling water bath until the volatile impurities hindering crystallization had been driven off. Conversely, in other experiments the oil crystallized before evaporation of the ether layer, on simple standing (for a few days) of the loosely stoppered flask containing the extract; partial evaporation of the ether layer above the oily liquid apparently caused the reaction product to separate from the ether solution in a crystalline form and promoted crystallization of the oil by seeding. In these cases a small amount of the oil nevertheless remained uncrystallized. In other cases, finally, crystallization could be initiated by simply placing the flask in a freezing mixture, although most commonly it was necessary to apply the vacuum crystallizing technique.

The crystalline product obtained by one method or another consisted of sticky, readily fusible crystals with a yellow color, the purification of which was an extremely difficult matter. The crystals obtained by the vacuum technique were washed out of the flask with hot alcohol, in which they dissolved readily. On cooling the alcoholic solution a small amount of material separated in the form of colorless crystals, but the greater proportion remained in the mother liquor, from which fresh portions of material could only be isolated with great difficulty, owing to partial esterification by the alcohol.

The product obtained in this experiment was recrystallized from benzene-alcohol mixture. From the hot solvent, however, the product separated in the form of an oil; it was therefore necessary to dissolve the substance in an excess of alcohol-benzene in the cold and to evaporate the resultant solution in vacuum. During fractional concentration of the solution, the first portions of substance were isolated in the form of colorless crystals, m.p. 97-100°. The main bulk of substance, however, which separated on further concentration of the solution, required a fresh recrystallization. After pressing on porous tile, this batch of crystals was recrystallized from pure ether in which it dissolved with very great difficulty. It was insoluble in other organic solvents. The total yield of crystalline product was 5.7 g, or 26.2% of theory, on the basis of the acid $C_8H_{10}O_5$. M.p. 98-100°.

B. Hydrolysis of the ethyl ester of 1-butoxycyclopropane-2-carboxylic acid. 1) Preliminary experiments: a) Action of 0.1 N sulfuric acid. No visible change occurs in the water-insoluble ester layer on boiling 2 g of the cyclic acid with 50 ml of 0.1 N sulfuric acid while stirring mechanically for one hour. Nevertheless, on treating the neutralized aqueous layer with an acetic acid solution of p-nitrophenylhydrazine, a precipitate of a p-nitrophenylhydrazone is formed, indicating partial hydrolysis of the ester under these conditions.

b) Action of 2 N sulfuric acid. Complete hydrolysis of the same quantity of ester was effected in an hour under the same conditions. After neutralization with 10% caustic alkali, the solution was concentrated by heating on a water bath in vacuum. The concentrated solution yielded a p-nitrophenylhydrazone melting at 196° after two crystallizations from alcohol and not suffering any depression of melting point when mixed with the p-nitrophenylhydrazone of the acid $C_8H_{10}O_5$.

2. Hydrolysis of the cyclic ester with 2N sulfuric acid and isolation of the products of hydrolysis. After 40.5 g (¼ mole) of the ester had been fully hydrolyzed by treatment with 330 ml of 2 N sulfuric acid under the conditions described above, the solution was neutralized with 10% caustic soda and extracted

with ether. The ether extracts were dried and fractionated: first fraction, b.p. 35-90°, 3.0 g; second fraction, b.p. 90-114°, 2.5 g; third fraction, b.p. 114-118°, 7.0 g.

Pure butyl alcohol, b.p. 117°, was isolated from the third fraction; the other two fractions were apparently mixtures of ethyl and butyl alcohols contaminated (first fraction) with ether.

The aqueous solution from which the ether extracts had been made was concentrated in vacuum on the water bath, and filtered under cooling from the precipitated mineral salts; to the cooled filtrate was added 15 ml concentrated sulfuric acid. The solution was subjected to prolonged extraction with ether in a Soxhlet. The acid $C_8H_{10}O_5$ separated in the form of an oil below the ether layer. Crystallization set in on partial evaporation of the ether layer.

The crude product was recrystallized from a mixture of benzene and alcohol by the previously described method, when the following fractions were obtained: 1) m.p. 100°, 1.6 g; 2) m.p. 98-100°, 5.0 g; 3) m.p. 98-100°, 1.5 g.

In all, 8.1 g of recrystallized product melting at 98-100° was obtained, equivalent to 34.8% of the theoretical yield. The yield of crude product was 12.6 g (54.4% of theory).

Summary of Experiments on the Hydrolysis with Sulfuric Acid of Butoxy-cyclopropane Carboxylic Acid and its Ethyl Ester

Expt. No.	Quantity of reagents				Yields of reaction products			
	Cyclic acid, g	0.1 N sulfuric acid, ml	Cyclic ester, g	2 N sulfuric acid, ml	Acid $C_8H_{10}O_5$		Butyl alcohol	
					g	% theory	g	% theory
1	15	200	–	–	2.5	26	4.8	70.0
2	41	300	–	–	5.7	23.6	16.0	83.3
3	35	250	–	–	5.4	26.2	13.5	82.3
4	–	–	43	400	5.0	25	–	–
5	–	–	46.5	300	8.1	34.8	–	–

The yields of acid $C_8H_{10}O_5$ in this table relate to the recrystallized product. On the average, with the exception of Experiment 5, they ranged about 25% of theory. In some experiments the yield of crude product, calculated on acid $C_8H_{10}O_5$, reached 75% of theory. The melting points of the acids obtained in experiments 1-5 ranged from 97 to 100° (after recrystallization). The yield of butyl alcohol might be increased by ether extraction of the aqueous distillates, which is evidence of complete hydrolysis of the acid or its ester under these conditions.

2. The Acid $C_8H_{10}O_5$ and Its Derivatives

The pure acid is a nearly colorless crystalline substance with m.p. about 100°. It is readily soluble in water and sparingly soluble in organic solvents with the exception of alcohol. In the latter, however, it partially esterifies on heating, (for purification by recrystallization, see above). It is neutralized in aqueous solutions with caustic alkalies in the cold and forms a silver salt. It gives the reactions for the aldehyde group (silver mirror, and reaction with Fehling's solution). The aqueous solutions yield, with the appropriate reagents, a semicarbazone and a p-nitrophenylhydrazone. The semicarbazone, m.p. 187-188°, is difficultly soluble in water. After two recrystallizations from water the melting point is raised to 197-198° (in a capillary with rapid heating of the bath); the p-nitrophenylhydrazone forms golden needles (from alcohol), m.p. 198° (with decomposition), insoluble in hot water. It was not possible to prepare an analytically pure specimen of the p-nitrophenylhydrazone.

Apart from the carbonyl group, the acid also contains a double bond: It adds on one mole H_2 on catalytic hydrogenation and decolorizes a chloroform solution of bromine. It reacts energetically with permanganate solution.

Analyses

0.1530 g substance: 0.2899 g CO_2; 0.0779 g H_2O.
0.1508 g substance: 0.2844 g CO_2; 0.0764 g H_2O.
Found %: C 51.68, 51.44; H 5.70, 5.67.
$C_8H_{10}O_5$. Computed %: C 51.61; H 5.42.

0.1528 g substance: 26.67 g acetic acid; Δ t 0.123°.
0.2342 g substance: 30.08 g acetic acid; Δ t 0.175°.
Found: M 185.0, 173.6.
$C_8H_{10}O_5$. Computed: M 186.1.

Neutralization equivalent:

0.1325 g substance: 14.7 ml 0.1 $\underline{N}$ NaOH (Φ = 0.9755).
0.1855 g substance: 20.7 ml 0.1 $\underline{N}$ NaOH (Φ = 0.9755).
0.1369 g substance: 15.3 ml 0.1 $\underline{N}$ NaOH (Φ = 0.9755).
Found: equivalent 92.41, 91.85, 91.73.
$(C_8H_8O)(COOH)_2$. Computed: equivalent 93.05.

Analysis of the silver salt of the acid:

0.1903 g substance: 0.1024 g Ag.
0.1509 g substance: 0.0808 g Ag.
Found %: Ag 53.80, 53.56.
$C_8H_8O_5Ag_2$. Computed %: Ag 53.96.

Analysis of the semicarbazone (m.p. 197-198°):

0.0502 g substance: 7.72 ml N_2 (16°, 748 mm).
0.1094 g substance: 15.92 ml N_2 (16°, 736 mm).
Found %: N 17.19, 17.06.
$C_9H_{13}O_5N_3$. Computed %: N 17.28.

Analysis of the p-nitrophenylhydrazone (m.p. 198-199° with decomposition):

0.1190 g substance: 9.9 ml N_2 (15°, 757 mm).
0.1120 g substance: 9.6 ml N_2 (17.5°, 742 mm).
0.1072 g substance: 9.2 ml N_2 (14°, 755 mm).
Found %: N 9.87, 9.87, 10.14.
$C_{14}H_{15}O_8N_3$. Computed %: N 13.08.

In explanation of the discrepency between the found and calculated contents of nitrogen in the p-nitrophenylhydrazone, we suggest the possibility of formation of the molecular compound $C_{14}H_{15}O_8N_3 \cdot 2C_2H_5OH$ (during crystallization of the hydrazone from alcohol), which has the calculated content N% 10.16. However, a Zeisel analysis convinced us of the absence of alcohol of crystallization in the molecule of this compound.

The nitrogen deficiency can be ascribed to the presence of impurities which do not separate during recrystallization of the substance.

Catalytic hydrogenation of the acid $C_8H_{10}O_5$:

0.9889 g substance: 0.1024 g Pt.
Found: 120.7 ml H_2 (0°, 760 mm).
$C_8H_{10}O_5$. Computed: 119.1 ml H_2 (0°, 760 mm).

Oxidation of acid $C_8H_{10}O_5$. Experiment 1. An aqueous solution of 14.9 g (0.08 mole) of the acid was oxidized in the cold with a 3% solution of potassium

permanganate.

After addition of 59.5 g KMnO$_4$ (in solution) the consumption of the oxidizing agent was rather slow; no further addition was made.

The solution of oxidation products was filtered off from the manganese dioxide, and the latter was washed with hot water. The filtrate together with the wash waters was subjected to distillation. A sample of distillate was poured into an acetic acid solution of p-nitrophenylhydrazine and revealed the absence from the distillate of carbonyl-containing, neutral products of oxidation. The remainder of the solution in the distillation flask was concentrated to a volume of 100 ml, acidified with the requisite amount of sulfuric acid (based on the amount of permanganate used in the reaction), and extracted with ether in a Soxhlet for 20 hours.

4.3 g of a solid acid obtained by extraction melted at 183°, and after a single crystallization from water it melted at 184-185°, which agrees with the m.p. of succinic acid. It did not depress the m.p. of an authentic sample of succinic acid.

The ethereal mother liquor remaining after the isolation of succinic acid was concentrated and yielded two further fractions of solid acid, the first with m.p. 170° (0.8 g) and the second with m.p. 180° in the case of the purer crystals (0.2 g). After recrystallization, both fractions were found to be identical with succinic acid.

A further prolonged extraction of the aqueous solution with ether led to the isolation of a further 0.4 g succinic acid. In all, the oxidation of 14.9 g of acid C$_8$H$_{10}$O$_5$ yielded 5.7 g of succinic acid, or 60% of the theoretical yield. No other crystalline dibasic acids were detected among the products of oxidation.

The combined mother liquors remaining after separation of the succinic acid did not amount to more than 5 ml. The last fractions of succinic acid were washed with ether after separation, and these lots of ethers were added to the main solution. The combined ethereal solutions were diluted with fresh ether, dried with anhydrous sodium sulfate, and worked up for extraction of the lower (fatty) acids. For this purpose the ether was distilled off on the water bath and the residue (a dark liquid in quantity of less than 1 g) was distilled on Wood's alloy. The distillate (b.p. 100-145°) was neutralized with caustic soda (to phenolphthalein), concentrated on the water bath, and to the cooled solution was added a solution of silver nitrate. The precipitated silver salts immediately darkened and were therefore unsuitable for analysis. The filtered-off solution was refluxed on the water bath until silver no longer separated out on standing. The resultant perfectly transparent solution, which was stable to light if not kept too long, was carefully concentrated in vacuum until a silver salt had precipitated. It was only possible to isolate and analyze a small amount of silver salt by this procedure:

0.0787 g substance: 0.0489 g Ag.
Found %: Ag 62.13.
C$_2$H$_3$O$_2$Ag. Computed %: Ag 64.66.

Lack of material prevented us from improving on this analysis.

Experiment 2. 6 g of acid C$_8$H$_{10}$O$_5$ was oxidized under the same conditions as in Experiment 1. Complete oxidation in the cold required 29 g of potassium permanganate. After acidification with sulfuric acid the aqueous solution of oxidation products, in contrast to the previous procedure, was subjected to steam distillation in order to separate the fatty acids (volatile in steam) from the succinic acid. The distillate was saturated with silver carbonate while heating on the water bath (6 hours) until the solution gave a neutral reaction. The

excess of silver carbonate was then filtered off and the solution concentrated in vacuum. As in the previous experiment, all of the fractions of silver salts were unsuitable for analysis.

The solution of acids non-volatile in steam was divided into two parts: one part, comprising about one-third of the total, was tested for oxalic acid (after removal of the sulfate ion) by treatment with calcium chloride solution. Separation of an insoluble precipitate of calcium oxalate was not observed, indicating absence of oxalic acid.

The remaining two-thirds was extracted with ether in a Soxhlet, when succinic acid was isolated. M.p. 184-185° after recrystallization from water.

Neutralization equivalent:

$$0.2057 \text{ g substance: } 39.8 \text{ ml } 0.1 \underline{N} \text{ NaOH } (\Phi = 0.876).$$
Found: equiv. 60.3.
$C_4H_6O_4$. Computed: equiv. 59.0.

Analysis of silver salt:

$$0.2442 \text{ g substance: } 0.1568 \text{ g Ag.}$$
$$0.2477 \text{ g substance: } 0.1586 \text{ g Ag.}$$
Found %: Ag 64.19, 64.04.
$C_4H_4O_4Ag_2$. Computed %: Ag 64.60.

SUMMARY

1. 1-Butoxycyclopropane-2-carboxylic acid is completely hydrolyzed with fission of the butoxyl group on heating with 0.1 $\underline{N}$ sulfuric acid, and its ethyl ester behaves in the same way with 2 $\underline{N}$ sulfuric acid.

2. Examination of the aqueous solutions obtained by hydrolysis of these compounds revealed the presence of butyl alcohol and an unsaturated dibasic aldehyde acid with the composition $C_8H_{10}O_5$.

3. Data from analysis and structural investigation of the acid with the composition $C_8H_{10}O_5$ enable it to be regarded as the product of crotonic condensation of two molecules of aldehydo-succinic acid.

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See CB translation p. a-173 ff.
See CB translation p. a-355 ff.
See CB translation p. a-527 ff.

# REACTIONS OF ALIPHATIC DIAZO COMPOUNDS WITH UNSATURATED COMPOUNDS

V. THE FORMATION OF ALDEHYDOSUCCINIC ACID AND ITS TRANSFORMATIONS DURING THE HYDROLYSIS OF 1-BUTOXYCYCLOPROPANE-2-CARBOXYLIC ACID

I. A. Dyakonov and N. A. Lugovtsova

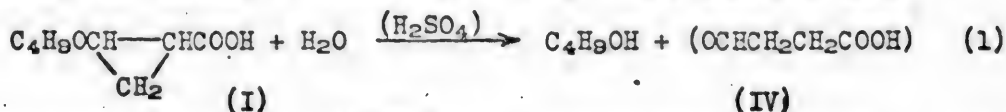Chemical Research Institute of Leningrad State University

In communication (IV) [1] it was shown that the hydrolysis of butoxycyclopropane-2-carboxylic acid and its ethyl ester

$$C_4H_9O-CH-CH-COOH \quad (I) \qquad C_4H_9O-CH-CH-COOC_2H_5 \quad (II)$$
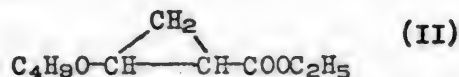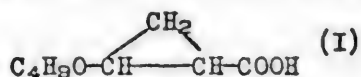
in the presence of solutions of sulfuric acid of various strengths yielded butyl alcohol [as well as ethyl alcohol in the hydrolysis of (II)] and a dibasic unsaturated aldehydo acid with the m.p. of 99-100°, and the composition $C_8H_{10}O_5$. On the basis of the analytical data for this acid and its derivatives, and of the formation of succinic acid during oxidation with permanganate, the following structural formula was proposed for the acid:

$$HOOC-CH_2-CH_2-CH=C-CH_2-COOH,$$
$$CH=O$$
$$(III)$$
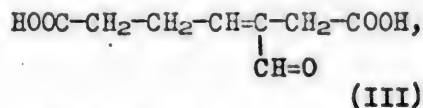
which enabled the acid $C_8H_{10}O_5$ to be regarded as the product of "crotonic" condensation of two molecules of aldehydosuccinic acid. In this connection the hypothesis was advanced that in the hydrolysis of compounds (I) and (II), aldehydosuccinic acid is actually formed in the first place but is converted into acid (III) during the heating of (I) and (II) with dilute sulfuric acid:

$$C_4H_9OCH-CHCOOH + H_2O \xrightarrow{(H_2SO_4)} C_4H_9OH + (OCHCH_2CH_2COOH) \quad (1)$$
$$CH_2 \qquad (I) \qquad\qquad\qquad (IV)$$

$$2(OCHCH_2CH_2COOH)-H_2O \xrightarrow{(H_2SO_4)} HOOCCH_2CH_2CH=CCH_2COOH \quad (2)$$
$$CHO$$
$$(III)$$

Both of the equations required experimental substantiation since up to now we have not succeeded in demonstrating the formation of aldehydosuccinic acid as an intermediate product of reactions (1) and (2), nor have we effected the transformation (2) with authentic aldehydosuccinic acid. Neither this transformation nor the aldehydo acid (III) itself [1,3] have been described in the literature by other authors.

For the purpose of detecting aldehydosuccinic acid in the hydrolysis products, tests were made on the acidic aqueous solutions which had served as media for the reaction. In some cases tests were performed on solutions obtained by incomplete hydrolysis or those obtained under conditions less drastic than usual [1] (for example, using 0.1 N sulfuric acid in the cold and stirring vigorously).
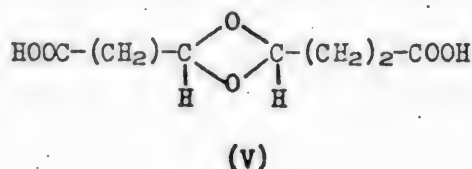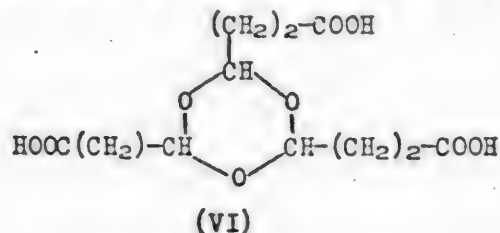
Tests were made with a sample of the p-nitrophenylhydrazone from a solution which had been neutralized with caustic alkali and concentrated (for removal of butyl alcohol). In not a single experiment, however, could aldehydosuccinic acid be detected in the solution by this method. In all cases the preparations of p-nitrophenylhydrazone had the melting point and composition required by the p-nitrophenylhydrazone of the aldehydo acid (III)*.

This result can only be reconciled with equations 1 and 2 with the aid of the hypothesis that the transformation of equation (2) takes place in the very instant of formation of the initial aldehydosuccinic acid. It could be imagined that a reduction in the velocity of this transformation, for instance by reducing the acidity of the medium to the minimum that would still permit hydrolysis to take place, would nevertheless make possible the separation of the required aldehydo-succinic acid from solution. The most satisfactory results along these lines were obtained by using 20% acetic acid. It was found that on heating butoxycyclopro-pane carboxylic acid with 20% acetic acid, the acid is hydrolyzed with formation in the solution of butyl alcohol and aldehydosuccinic acid. Under these condi-tions the latter does not generally undergo visible changes.

We characterized aldehydosuccinic acid in the form of its trimer, as well as by preparation of its semicarbazone and p-nitrophenylhydrazone. The melting point [2] and composition of these derivatives differ markedly from those of the corresponding derivatives of the aldehydo acid (III). Apart from analyses, both of the derivatives of aldehydosuccinic acid, as well as the trimer, did not de-press the melting point of the corresponding authentic specimens.

Authentic aldehydosuccinic acid was prepared by the method of Carriere and Wislicenus [4,5] starting from formyl succinic ester.

Two formulas are proposed in the literature for the polymer of aldehydosuc-cinic acid: a dimer (Harries [6,7] (V)) and a trimer (Cariere [4] (VI)):

$(CH_2)_2-COOH$

CH

$HOOC(CH_2)-CH$ $CH-(CH_2)_2-COOH$

(VI)

$HOOC-(CH_2)-C$ $C-(CH_2)_2-COOH$ H H

(V)

Molecular weight determinations of the polymer prepared by us both in the ab-sence and in the presence of sulfuric acid, as well as determinations on various specimens of aldehydeosuccinic acid prepared by a variety of methods, confirmed the trimer formula.

There is also a discrepancy between the melting points of the trimer in the literature. Harries and other workers [2,6,7] give a m.p. of 147°, while Car-riere [4] gives 167°. The latter's high value may have been the result of his special method of melting (rapid heating on a mercury bath). We obtained an in-itial m.p. of 147°.

The analytical data (empirical analysis, neutralization equivalent, and molecular weight) for the preparation with the above melting point were entirely satisfactory. A little later we found that under certain conditions of crystal-lization a preparation could be obtained which had a melting point of 155° when heated rapidly in a capillary.

See also Communication IV of this series, CR translation p. 2109.

In the hydrolysis experiments with acetic acid we also succeeded in isolating in good yield the free monomeric aldehydosuccinic acid, purified by distillation. We believe, however, that the obtained acid is contaminated with the original butoxycyclopropane carboxylic acid, judging by the variable boiling point and the high neutralization equivalent of the liquid acid remaining after polymerization of the main bulk of aldehydosuccinic acid. In many cases, moreover, polymerization of the acid commenced immediately after its distillation, and this also interfered with the examination of the monomer. A summary of experiments on hydrolysis in acetic acid and on the preparation of aldehydosuccinic acid by this method is given in Table 1.

Having at our disposal preparations of aldehydosuccinic acid (and its trimer) we were able to study its behavior on heating in sulfuric acid, which was necessary, bearing in mind equation (2). Aldehydosuccinic acid was therefore heated with solutions of 0.1 N and 2 N sulfuric acid for a fairly long time [the same concentrations of acid were used in the hydrolysis of butoxycyclopropane carboxylic acid (I) and its ethyl ester (II)].

The heating did not result in any change in the aldehydosuccinic acid in sulfuric acid solution, as demonstrated by the recovery of the trimer from the monomeric acid which had been extracted with ether, and also by the p-nitrophenylhydrazone test. The p-nitrophenylhydrazone was prepared from acid solution after neutralizing it with sodium acetate and not with caustic alkali, in contrast to the procedure for testing solutions prepared after hydrolysis of ester (II) and acid (I).

On the basis of these experiments it can be concluded that sulfuric acid does not in general promote the transformation of aldehydosuccinic acid as outlined in equation (2). We may consequently make two mutually exclusive inferences: either the acid $C_8H_{10}O_5$ is generally not a product of crotonization of aldehydosuccinic acid, the presence of which has still not been established among the products of hydrolysis with sulfuric acid, or the process of crotonization takes place under the conditions of heating of the alkali-neutralized solution. This operation, as already noted, followed directly on the neutralization with caustic alkali of the acidic aqueous solution of the products of hydrolysis.

We decided upon the second alternative in the course of this investigation. This decision was prompted by the fact that neutralization of the sulfuric acid solution of aldehydosuccinic acid not with caustic alkali but with sodium acetate (in the experiments with authentic aldehydosuccinic acid or its trimer) enabled us to obtain its p-nitrophenylhydrazone and not the p-nitrophenylhydrazone of acid (III), as was the case in the experiments on the hydrolysis of the cyclic compounds (I) and (II). This observation, important for the study of the mechanism of formation of acid (III), was used in the investigation of the products of hydrolysis of cyclopropane derivatives.

In this case also experiment showed that the employment of sodium acetate or calcium carbonate during neutralization gives the possibity of preparation of the p-nitrophenylhydrazone of aldehydosuccinic acid. After a number of unsuccessful attempts, the free aldehydosuccinic acid was also isolated from sulfuric acid solution and was characterized in the form of its trimer. **

We thus obtained a missing link in the scheme of equations (1) and (2), i.e. aldehydosuccinic acid as an intermediate product in the formation of aldehydo acid

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In these experiments we did not use monomeric aldehydosuccinic acid but its trimer. It was established that the latter readily depolymerized on heating with 0.1 N or 0.2 N sulfuric acid.

** Neither in this case nor in the experiments with acetic acid was it possible to purify the aldehydosuccinic acid by distillation and to determine its constants, owing to the polymerizing and resinifying action of sulfuric acid, traces of which apparently contaminated aldehydo acid.

(III). This scheme should now only be corrected in the sense that the crotonic condensation of aldehydosuccinic acid proceeds (equation (2) not in presence of acid, but apparently under the conditions of heating of the aqueous solution of its sodium or potassium salt. As pointed out above, immediately after this operation the acid (III) was identified in the solution by the semicarbazide and p-nitrophenylhydrazine tests.

Final confirmation was provided by the following experiments: the acidic aqueous solution of the products of hydrolysis of the ester (II) with $2N$ sulfuric acid was divided into two equal portions. One portion was neutralized with 10% potassium hydroxide solution, and the other portion by heating on the water bath with calcium carbonate. Both solutions were then concentrated to a small volume for preparation of the semicarbazones, which were isolated by treatment of calculated amounts of the solutions of semicarbazide hydrochloride with the test solutions. The semicarbazone obtained from the first sample was that of the aldehydo acid (III), while the semicarbazone from the second sample was that of aldehydosuccinic acid (IV). The results were confirmed by analysis and determination of the melting point in admixture with authentic derivatives of both acids.

The transformation represented by equation (2) was also realized by us with a solution of the sodium salt of authentic aldehydosuccinic acid prepared by hydrolysis of acid (I) with acetic acid. Heating of an exactly neutralized solution of acid (IV) led to formation of the aldehydo acid (III) in a yield of 37% which even exceeded the yield of this acid in the experiments on hydrolysis of the cyclopropane derivatives. The use of excess of alkali did not improve the results. In this case it was impossible to isolate acid (III) in the pure state, owing to progressive resinification, although its formation in solution was here also established by the preparation of its semicarbazone (25% yield, analysis corresponded to the theoretical requirements).

It was also shown that the sodium salt of the trimer of aldehydo acid $(C_4H_5O_3Me)_3$ does not undergo a similar transformation in aqueous solutions, which was of course to be expected in view of the absence of carbonyl functions in this compound. Similarly, the calcium salt of monomeric aldehydosuccinic acid does not change to an appreciable extent when its aqueous solution is heated. An analogous observation was made, as already recalled, during the preparation of the semicarbazone of aldehydosuccinic acid from a solution neutralized with calcium carbonate.

EXPERIMENTAL

I. Transformation of 1-Butoxycyclopropane-2-carboxylic Acid Into Aldehydosuccinic Acid by the Action of Acetic Acid

a) Semicarbazone of aldehydosuccinic acid. 2 g of the cyclic acid and 20 ml of 20% acetic acid were heated to boiling for 3 hours under a reflux condenser. The water and acetic acid were then distilled off in the vacuum of a water jet pump while heating on the water bath. The undistilled residue was mixed with a solution of semicarbazide acetate (1.3 g semicarbazide hydrochloride and 25 g sodium acetate). The semicarbazone of aldehydosuccinic acid was obtained in the amount of 1 g (50% of the theoretical yield). After a single recrystallization from water the m.p. was 178-179°, in agreement with the value of Harries [2]. It did not depress the melting point of an authentic specimen of the semicarbazone (see I, d). The semicarbazone was titrated with caustic alkali in aqueous solution.

0.1727 g substance: 39.5 ml N_2 (18°, 750 mm).
0.0713 g substance: 16.3 ml N_2 (18°, 748.5 mm).
Found %: N 26.48, 26.44.
$C_5H_8O_3N_3$. Computed %: N 26.31.

Neutralization equivalent:

$$0.1806 \text{ g substance: Consumed } 13.9 \text{ ml NaOH } (\mathfrak{T} = 0.802).$$

Found: equiv. 161.5.

$C_4H_8ON_3CO_2H$. Computed: equiv. 159.6.

b) p-Nitrophenylhydrazone of aldehydosuccinic acid. 2 g of the cyclic acid was treated with 20 ml of 20% acetic acid as described in I, a. Following the removal of the water and acetic acid in vacuum, a solution of p-nitrophenylhydrazine was added to the undistilled residue. After crystallization from hot water the p-nitrophenylhydrazone of aldehydosuccinic acid melted at 177° in agreement with Harries [2]. The mixture with authentic p-nitrophenylhydrazone (see I, d) was not depressed in melting point.

0.1055 g substance: 16.12 ml N_2 (16°, 736 mm).

Found %: N 17.48.

$C_{10}H_{11}O_4N_3$. Computed %: N 17.71.

The preparation of an analytically pure preparation of the p-nitrophenylhydrazone proved to be extremely difficult.

Following Carriere's procedure [4], we used ethyl alcohol as the solvent for recrystallization, but thereby obtained a preparation (m.p. 177°) with a low nitrogen content (16.40, 16.37%).

The use of methyl alcohol gave even less satisfactory results, (m.p. 176-177°, nitrogen content 15.48, 15.55%).

It is necessary to filter the hot solution during recrystallization from water because otherwise values deviating from theory are likewise obtained. Unfortunately the melting point of the preparation is not a reliable criterion of its purity, since in all cases the recrystallized preparation melted (usually) within the range of 176 to 178°.

c) Aldehydosuccinic acid and its trimer. 28 g of cyclic acid and 235 ml of 20% acetic acid were boiled for 3 hours while stirring. The acetic acid, water and butyl alcohol were distilled off in a 110 mm vacuum (b.p. 55-64°). The residue in the distilling flask was distilled at 8 mm. B.p. 123-128° at 8 mm. A thick, viscous liquid, polymerizing on standing: $n_\alpha^{22.8}$ 1.44644.

Literature data for aldehydosuccinic acid: b.p. 134-136° at 14 mm [7]; 143-145° at 16-20 mm [2]; 142-143° at 15 mm [4]; n_α^{23} 1.45475 [6]; n_α^{23} 1.44571 [7].

Further investigations (see below) showed that the aldehydosuccinic acid prepared by us was not entirely free from impurities. However, the trimer into which the acid is transformed on storing can be isolated in the analytically pure state. During this transformation part of the acid remains unpolymerized and may be separated from the solid trimer by filtration. After crystallization from water the trimer melted at 146.5-147.5° and the mixed melting test with the trimer of authentic aldehydosuccinic acid (see I, d) did not show a depression. Yield of recrystallized preparation 4.5 g (25% of theory).

0.1342 g substance: 0.2282 g CO_2; 0.0734 g H_2O.

0.1378 g substance: 0.2342 g CO_2; 0.0756 g H_2O.

Found %: C 46.37; 46.36; H 6.12, 6.14.

$[C_4H_8O_3]_3$. Computed %: C 47.06; H 5.98.

The low value for carbon may be ascribed to the presence of a little succinic acid. After repeated crystallization from water the following analytical results were obtained:

0.1116 g substance: 0.1910 g CO_2; 0.0596 g H_2O.

Found %: C 46.70; H 5.97.

$[(C_3H_5O)CO_2H]_3$. Computed %: C 47.06; H 5.98.

Neutralization equivalent:

$$0.1978 \text{ g substance: } 19.1 \text{ ml NaOH } (\Phi = 1.005).$$
$$0.1526 \text{ g substance: } 14.7 \text{ ml NaOH } (\Phi = 1.005).$$

Found: equiv. 103.0, 103.3.

$[(C_3H_5O)CO_2H]_3$. Computed: equiv. 102.0.

Cryoscopic determination of molecular weight:

$$0.2248 \text{ g substance: } 21.86 \text{ g acetic acid: } \Delta t\ 0.13.$$
$$0.2331 \text{ g substance: } 20.63 \text{ g acetic acid: } \Delta t\ 0.15.$$

Found: M 308.4, 294.0.

$(C_4H_6O_3)_3$. Computed: M 306.0.

The non-polymerizing residue of acid is apparently a mixture of aldehydo-succinic acid and the initial cyclic acid.

Neutralization equivalent:

$$0.2400 \text{ g substance: } 22.2 \text{ ml NaOH } (\Phi = 0.804).$$
$$0.3660 \text{ g substance: } 33.5 \text{ ml NaOH } (\Phi = 0.804).$$

Found: equiv. 134.7, 135.8.

$(C_3H_5O)CO_2H$. Computed: equiv. 102.0.
$(C_7H_{13}O)CO_2H$. Computed: equiv. 158.0.

On adding a drop of concentrated sulfuric acid to the mixture of acids, the polymerization of the aldehydosuccinic acid present in admixture with butoxycyclo-propane carboxylic acid is accelerated, a considerable amount of trimer separating out after only 24 hours. During this process the butoxycyclopropane carboxylic acid apparently decomposes, judging by the odor of butyl alcohol.

Summary of Experiments on Hydrolysis of Butoxycyclopropane
Carboxylic Acid in Presence of Acetic Acid

Expt. No.	Butoxycyclo-propane carb-oxylic acid, g	20-25% acetic acid, ml	Duration of heat-ing, hours	Aldehydosuccinic acid *		Trimer $(C_4H_6O_3)_3$ Yield **	
				Yield, % of theory	Boiling point	(g)	% of theory
1	28	235	3	69.2	123-128° at 8 mm	4.5	25
2	33	250	1	80.3	145-153 21	–	–
3	37.5	250	1	76.9	131-139 9	5.1	21
4	18.5	100	5	92.9	132-143 10	3.45	29

d) Authentic aldehydosuccinic acid and its derivatives. For comparison purposes aldehydosuccinic acid was prepared by Carriere's method [4] — the action of oxalic acid on formylsuccinic ester [5]. The yield of aldehydosuccinic acid with b.p. of 125-136° at 10-17 mm was 47% of theory, calculated on the formyl-succinic ester. After a second distillation the main bulk came over at 130-133° at 8 mm, but a part of the product polymerized in the distilling flask.

The trimer of aldehydosuccinic acid obtained by polymerizing the fraction

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The varying yields of aldehydosuccinic acid in experiments 1-4 and the inconstancy of its boiling point can be explained by the varying content of the original cyclic acid in the crude reaction product (see above). Pure aldehydosuccinic acid could not be separated from the mixture, but its trimer was obtained in the analytically pure form.

** The yields of trimer are based on the pure, recrystallized preparation and calculated on the amount of butoxycyclopropane carboxylic acid taken into reaction. In these columns no account is taken of the supplementary amounts of trimer which are obtained on adding sulfuric acid to the non-polymerizing residue of crude reaction product.

boiling at 130-133° (8 mm) melted at 147° after crystallization from water. Recrystallization from water was promoted by scratching the side of the vessel with a glass rod; the melting point was determined by the usual method (see II, C). Semicarbazone, m.p. 178° (from water); p-nitrophenylhydrazone, m.p. 177° (from water).

II. Conversion into Aldehydosuccinic Acid by the Action of Sulfuric Acid of Various Concentrations on Butoxy-cyclopropane Carboxylic Acid and Its Ester

A) p-Nitrophenylhydrazone. 5.5 g of butoxycyclopropane carboxylic acid was boiled with 75 ml of 0.1 N sulfuric acid until oily drops of the acid disappeared from the solution and the solution had become perfectly transparent.

The cooled solution was then concentrated in vacuum to a volume of 25 ml. To 10 ml of this solution was added a solution of p-nitrophenylhydrazine acetate (0.7 g) and the precipitated p-nitrophenylhydrazone was filtered off, washed with acetic acid and then with water, and dried in vacuum over sulfuric acid. M.p. 175-176°. The melting point of the mixture with an authentic specimen of the p-nitrophenylhydrazone of aldehydosuccinic acid (m.p. 177°, see I, d) was 177-178°. Golden platelets were formed on slow cooling of the solution.

0.0614 g substance: 9.5 ml N_2 (17.5°, 751 mm).
0.0711 g substance: 11.3 ml N_2 (21°, 748 mm).
Found %: N 17.98, 18.17.
$C_{10}H_{11}O_4N_3$. Computed %: N 17.72.

5 g cyclic acid was stirred at ordinary temperature with 30 ml of 0.2 N sulfuric acid for 3 hours. The oily layer of acid that had not entered into the hydrolysis reaction was separated from the aqueous solution which was then further tested with the acetic acid solution of p-nitrophenylhydrazine for the presence of aldehydosuccinic acid. Addition of the reagent was immediately followed by separation of a p-nitrophenylhydrazone which after recrystallization from alcohol melted at 176°. It did not depress the melting point of the authentic p-nitrophenylhydrazone.

B) Semicarbazones $C_5H_9O_3N_3$ and $C_9H_{13}O_5N_3$. 2.3 g (0.05 mole) ethyl ester of butoxycyclopropane carboxylic acid and 100 ml of 2 N sulfuric acid were heated to boiling for 3 hours with rapid mechanical mixing. Heating was stopped after formation of a homogeneous, nearly transparent solution; the reaction mixture was cooled and divided into two equal portions which were treated as described below under 1) and 2).

1) Semicarbazone $C_5H_9O_3N_3$. To the first half of the solution (55 mm) was added 8 g of calcium carbonate in order to remove the sulfate ion. The calcium sulfate was filtered off and to the solution was added a further 3 g of calcium carbonate, and the solution heated for 4 hours on the water bath under a reflux condenser until the reaction to litmus was neutral. The unreacted calcium carbonate was filtered off and the filtrate concentrated on the water bath to a volume of 15 ml. To the concentrated neutral solution was added a solution of 2.6 g semicarbazide hydrochloride in 10 ml water. This was at once followed by separation of the semicarbazone of the aldehydosuccinic acid with m.p. 176° after recrystallization from water.

0.0709 g substance: 16.0 ml N_2 (20°, 753 mm).
0.0614 g substance: 13.8 ml N_2 (18°, 752 mm).
Found %: N 26.05, 26.08.
$C_5H_9O_3N_3$. Computed %: N 26.31.

2) Semicarbazone $C_9H_{13}O_5N_3$. To the second half of the solution (55 ml; see II, C) was added a 10% solution of potassium hydroxide until the reaction to

phenolphthalein was neutral, and the solution was then concentrated on the water bath to a volume of 15 ml. To the solution, after cooling and filtering off the separated mineral salts, was added a solution of 2.5 g semicarbazide hydrochloride in 10 ml water. This was immediately followed by precipitation of a semicarbazone which, after recrystallization from water, melted at 197-198°. A mixture with the semicarbazone of the crystalline acid $C_8H_{10}O_5$ melted at the same temperature.

0.0692 g substance: 10.5 ml N_2 (21°, 748 mm).
Found % N 17.34.
$C_8H_{13}O_5N_3$. Computed %: N 17.28.

C) <u>Trimer of aldehydosuccinic acid.</u> 8 g (0.05 mole) butyoxycyclopropane carboxylic acid was hydrolyzed by heating with 2.5% sulfuric acid. At the conclusion of the hydrolysis the solution was concentrated in vacuum to a volume of 30-35 ml and then extracted with ether in a Soxhlet for 20 hours. The ether was distilled off from the ether extract and the residue of thick, viscous liquid placed in a vacuum desiccator for removal of residual ether and water. After standing for a few days the aldehydosuccinic acid had polymerized to trimer. Yield of crude product 4.8 g (95% of theory). After solution in hot water and slow and tranquil cooling of the solution, red clusters of needles separated which melted in a capillary placed in a bath heated to 145°; on heating slowly, they melted at 148-150°.

If the capillary was placed in a hot bath and the temperature rapidly raised, the melting point rose to 155°. Conversely, on slowly raising the temperature of the sulfuric acid bath from 40° while the sample was immersed, the melting point was 146-148°. We ascribed to this substance the formula of the trimer $(C_4H_6O_3)_3$ on the basis of the analytical data and of determinations of the mixed melting point with the trimer obtained by hydrolysis of butoxycyclopropane carboxylic acid in an acetic acid medium.

0.1512 g substance: 16.7 ml NaOH.
0.2560 g substance: 28.2 ml NaOH.
Found: equiv. 103.4, 103.6
$C_4H_6O_3$. Computed: equiv. 102.1.

0.1057 g substance: 34.81 g acetic acid: Δ t 0.04.
Found: M 296.1.
$(C_4H_6O_3)_3$. Computed: M 306.0.

The mother liquor remaining after recrystallization of the crude reaction product was also examined. After concentration on the water bath it yielded a thick, partially crystallizing liquid. Addition of a drop of sulfuric acid accelerated polymerization. The thick, viscous mass of crystals resulting from polymerization was washed with alcohol and then with ether on the filter. The dried crystals melted at about 100°. A single recrystallization raised the melting point to 147° (with rapid heating). Repeated recrystallization yielded small, lustrous needles with m.p. 155° (on rapid heating of the capillary). The product was identical with the trimer.

The above-described relations between melting point and speed of rise of temperature during melting point determinations were also observed for those samples of this preparation which were prepared previously. It was found that the method of crystallization of the substance from water had a profound influence upon the melting temperature.

The trimer of aldehydosuccinic acid appears readily to form supersaturated aqueous solutions. If crystallization of such a solution is initiated by scratching the walls of the vessel with a rod, an amorphous mass of fine crystals comes down, melting generally, even with rapid rise of temperature, at about 147°

(rarely at about 150°). If, on the other hand, such a solution is allowed to stand without seeding, crystallization does not start at once (sometimes not before 24 hours), but the crystals come down in the form of well-developed clusters of small lustrous needles with m.p. 153-155° when rapidly melted, and about 148° when slowly melted.

III. Study of the Mechanism of Formation of the Acid $C_8H_{10}O_5$

A) Action of solutions of sulfuric acid on the trimer of aldehydosuccinic acid. 1) Action of 2 N sulfuric acid. Experiment 1. A solution of 1.3 g trimer $(C_4H_6O_3)_3$ in 20 ml of 2 $\underline{N}$ sulfuric acid was boiled for 2 hours under a reflux condenser. After cooling and neutralization with sodium acetate, a solution of p-nitrophenylhydrazine acetate was added. The precipitated p-nitrophenylhydrazone, after filtration, washing with dilute acetic acid, and drying in the desiccator, had m.p. 174°. A mixed melting point sample with authentic p-nitrophenylhydrazone of aldehydosuccinic acid (m.p. 177°) did not show any depression.

Experiment 2. A solution of 2 g trimer in 25 ml 2N sulfuric acid was boiled for 2 hours under a reflux condenser. Ether extraction of this solution in the Soxhlet yielded a small quantity of liquid polymerizing to the trimer of aldehydosuccinic acid when kept in the vacuum desiccator. After crystallization from water it was shown by the mixed melting point determination to be identical with authentic trimer of aldehydosuccinic acid.

2) Action of 0.1 N sulfuric acid. 2.8 g trimer was heated with 30 ml 0.1 $\underline{N}$ sulfuric acid for 2 hours. Ether extraction of this solution in the Soxhlet yielded a small amount of liquid which on treatment with solution of p-nitrophenylhydrazine acetate gave the p-nitrophenylhydrazone of aldehydosuccinic acid. M.p. 178° after crystallization from hot water.

B. Transformation of the sodium salt of aldehydosuccinic acid in aqueous solution. 1) Experiment in presence of caustic alkali. A solution of 13.8 g aldehydosuccinic acid (prepared by hydrolysis of butoxycyclopropane carboxylic acid; b.p. 147-153° at 21 mm) in 100 ml of 10% sodium hydroxide was refluxed for 2.5 hours. Neutralization of the cooled solution with 10% sulfuric acid showed that the excess of alkali in the initial solution was not large: neutralization (to phenolphthalein) required 1.5 ml 10% sulfuric acid.

The neutralized solution was concentrated on the water bath to a volume of 55 mm. After cooling, addition was made to one quarter of this solution of 1 g semicarbazide hydrochloride dissolved in a little water. The precipitated semicarbazone was filtered, washed with water and dried in a vacuum desiccator. Yield 0.36 g (25% of theory, calculated on the semicarbazide). M.p. 188-188.5° (unrecrystallized product). After one crystallization from water, the determined content of nitrogen corresponded to that calculated for the semicarbazone of the crystalline acid $C_8H_{10}O_5$.

0.0704 g substance: 11.0 ml N_2 (24°, 740.7 mm).
0.0696 g substance: 10.5 ml N_2 (17.5°, 748 mm).
Found %. N 17.50, 17.46.
$C_9H_{17}O_7N_3$. Computed %: N 17.28.

The remaining three-quarters of the solution, after acidification with 5 ml concentrated sulfuric acid, was extracted with ether in the Soxhlet. The acid $C_8H_{10}O_5$ was obtained from the ether extract in the form of an oil insoluble in ether, which is a characteristic sign of the formation of this acid (see Communication IV).

Unfortunately, this acid could not be isolated in the crystalline form using the methods previously applied by us for the preparation of this acid (see Communication IV). The cause of this failure is either overheating during drying

of the oil in vacuum or the presence of crystals of impurities, the formation of which could result from the increased alkalinity of the solution of aldehydosuccinic acid during the concentration of the sodium salt.

2) **Experiment in a neutral medium.** For the purpose of obtaining an aqueous solution of aldehydosuccinic acid, 2.5 g trimer was subjected to hydrolysis by heating with 25 ml of 2% sulfuric acid (see III, A). After heating for 2 hours, the solution was neutralized with 10% caustic soda (to phenolphthalein) and refluxed for 2 hours to complete the condensation reaction. The solution was then acidified with sulfuric acid and extracted with ether in the Soxhlet.

A thick yellow oil was seen to separate from the ether extract and to collect at the bottom of the flask. The oily product was separated from the ether layer which was evaporated in a crystallizing flask. Evaporation of the ether left a small amount of oily liquid which was combined with the main product of the reaction. The substance was observed to crystallize when kept in a vacuum. Gentle heating on the water bath led to complete solidification, but the product yellowed slightly. After crystallization from alcohol, washing with ether and pressing on porous tile, the crystals melted at 97-100°. The mixed melting point with the acid $C_8H_{10}O_5$ obtained by hydrolysis of the ester of butoxycyclopropane carboxylic acid (Communication IV) did not exhibit any depression. Yield 0.85 g (37% of theory, calculated on the initial trimer).

C) **Heating of the sodium salt of the trimer of $C_4H_6O_3$ in aqueous solution.** An aqueous solution of 0.3 g of trimer was neutralized with 3% sodium hydroxide (to phenolphthalein) and the neutral solution refluxed for 1.5 hours. The solution was then acidified with the requisite amount of sulfuric acid, and the resultant voluminous white precipitate was filtered off, washed with water and dried. Weight 5.12 g. M.p. 70-80°. It did not give the reaction for the carbonyl group and did not decolorize permanganate solution, indicating the absence of contamination with the crystalline acid $C_8H_{10}O_5$, (see Comunication IV). After two crystallizations from water the crystals melted at 147°. No melting point depression in admixture with an authentic specimen of trimer of aldehydosuccinic acid.

The solution filtered off from the crude trimer with m.p. 70-80° was also examined. It was subjected to ether extraction in a Soxhlet. After evaporation of the ether from the ethereal extract, there remained a small quantity of crystals which, after washing with ether and drying, melted at 133-136°. A single crystallization from water raised the melting point to 147°. The crystals were identified by a mixed melting point test with authentic trimer.

Formation of the acid $C_8H_{10}O_5$ in this experiment was not observed.

SUMMARY

1. It was shown that aldehydosuccinic acid is formed on hydrolysis of 1-butoxycyclopropane-2-carboxylic acid in a medium of 20% acetic acid.

2. It was shown that aldehydosuccinic acid is also the end product of reaction of 1-butoxycyclopropane-2-carboxylic acid and its ethyl ester with sulfuric acid solutions.

3. A study was made of the mechanism of formation of the previously described acid $C_8H_{10}O_5$. Formation of this acid is found to result from condensation of two molecules of aldehydosuccinic acid, on the lines of the crotonic condensation, on heating an aqueous solution of its sodium salt. This result is consistent with earlier data [1] on the determination of the structure of the dibasic aldehydo acid.

4. Formation of the acid $C_8H_{10}O_5$ was not observed on heating the aqueous

solution of the calcium salt of aldehydosuccinic acid and the aqueous solution of the sodium salt of the trimer of this acid.

5. Revised values are obtained for several data relating to characterization of the polymer of aldehydosuccinic acid, its semicarbazone, and its p-nitrophenylhydrazone.

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[*] See CB translation p. 2109 ff.
[**] See CB translation p. a-527 ff.

SYNTHESIS OF VINYL ALKYL ETHERS FROM ACETALS AND THEIR PROPERTIES

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The cleavage of an alcohol from acetals of carbonyl-containing compounds according to the scheme

$$\text{>CH-CH(OR)}_2 \longrightarrow \text{>C=CH(OR)- + ROH,}$$

constitutes a simple and convenient method, and frequently the only one, for synthesis of α,β-unsaturated (vinyl) ethers [1]. Thus, for instance, α- and α,β-. substituted vinyl alkyl ethers of the type of $-CH=C(OR)R'$ can be readily prepared by simply heating the acetals of ketones with a small amount of p-toluene sulfonic acid [2-4]. It has not been possible, however, by this method to split off an alcohol from acetals of aliphatic aldehydes [3,4].

Claisen [1,5] found that acetals of aldehydes lose a molecule of alcohol on heating with a mixture of quinoline and phosphorus pentoxide. This is not a convenient method, however, for the preparation of vinyl alkyl ethers, since their yields are low and the method itself, as admitted in so many words by the author, is lengthy and tedious. Other authors [4,6] have also remarked upon the unsuitability of this method for preparation of vinyl alkyl ethers. It has been reported [7,9] that cleavage of an alcohol from acetals of aldehydes with formation of vinyl alkyl ethers takes place on passing their vapors over hot metals or their oxides. On the basis of this reaction a series of patents [10] has been taken out on the synthesis of vinyl alkyl ethers by passing the vapors of acetals at 200-350° over catalysts (Ag, Au, Pt with various admixtures). Compare also [11, 12].

The formation of α,β-unsaturated ethers from acetals under the influence of traces of mineral acids was first observed by A.E.Arbuzov [13] and other Russian chemists [14,15]. Thus, for instance, it was pointed out, without citation of experimental data, that diethylacetal readily splits off alcohol in the presence of crude sulfanilic acid containing traces of H_2SO_4 [15].

We have found that aldehyde acetals smoothly split off a molecule of alcohol on heating with a small amount of sodium bisulfate, sulfanilic acid or aniline sulfate (in that order of decreasing catalytic activity) according to the scheme:

$$\frac{R'}{R''}\text{CH-CH}\frac{OR}{OR} \longrightarrow \text{ROH} + \frac{R'}{R''}\text{C=CHOR}$$

(R', R" = H or alkyl).

By this route we synthesized a series of vinyl alkyl ethers, including β-alkyl-

substituted members which are not readily accessible by other methods. The reaction is effected by simple boiling of the acetal in presence of the catalyst with simultaneous distillation in a column of the resultant vinyl alkyl ether and alcohol which have lower boiling points than the acetal. The vinyl alkyl ether content of the condensate (from analytical data) corresponds to yields exceeding 80% of the theoretical, calculated upon the reacted acetal. However, the isolation of the pure ethers from the condensate, which is a ternary mixture (alcohol + + ether + acetal) entails losses which reduce the yields to 55-70% (see table). In the case of vinyl ethyl ether the yield after one operation is rather lower (50%, or 69% on the basis of reacted acetal, since about 25% of the acetal comes over as an azeotrope with the alcohol and ether formed). In the table are listed the physical constants determined for all of the vinyl alkyl ethers obtained by this method. The determinations were made on the carefully purified compounds which were analyzed by the method of hydrolytic oximation [16]. All the ethers described contain 99.6-100% ± 0.2% pure substance.° The table also gives values of the molecular refractions and parachors found from these data and the corresponding computed values. The parachor was calculated by the method of group values (the standard value of the (C)=CH-(O) group is 33.5 [17], the correction for the γ-carbon atom is 0.7).

EXPERIMENTAL

The acetaldehyde acetals were prepared by the method described by us [18]. The diethylacetals of propionic, butyric, and isobutyric aldehydes were prepared by condensation of ethyl alcohol with the corresponding aldehydes in presence of hydrogen chloride.

Preparation of the vinyl alkyl ethers was effected in the following manner. 0.5-1 mole of the appropriate acetal and 0.2-1.5 g catalyst were placed in a two-necked 0.5-liter distillation flask attached to a column with glass packings and having an efficiency of about 15 theoretical plates. In the case of low-boiling acetals, pulverized fused $NaHSO_4$ is more convenient, and for high-boiling ones, $p-NH_2C_6H_4SO_3H$ or $(C_6H_5NH_2)_2 \cdot H_2SO_4$. Preparation of high-boiling vinyl alkyl ethers is more successful when carried out under reduced pressure. The reaction mixture is distilled under such conditions that the temperature of the vapors of condensate is as low as possible and in no circumstances higher than the boiling point of the split-off alcohol. The catalyst sometimes loses its activity and a fresh batch must be introduced. A small quantity of solid caustic alkali is placed in the receiver to avoid the possibility of combination of the alcohol with the ether. During fractionation of the condensate in the column, in most cases the pure ether does not come over, but instead its azeotrope with a small amount of the alcohol (compare [19]). Further purification of the vinyl alkyl ether is effected in the usual manner [17].

We shall now describe the synthesis of some of the vinyl alkyl ethers which we obtained.

Vinyl ethyl ether. 110.0 g (0.93 mole) diethylacetal was distilled over 0.7 g $NaHSO_4$. At 63-71° (mainly at 67-71°) 100.8 g condensate came over and on fractionation (755 mm) yielded 36.9 g vinyl ethyl ether with b.p. 35.3-36.0° (yield 55%). It was washed with water, dried over potassium carbonate and sodium and again distilled to give 35.0 g pure substance with b.p. 35.8° (763.5 mm). In addition to the vinyl ethyl ether there were obtained 11.8 g unchanged acetal with b.p. 101.5-102.5° and 45.2 g of a fraction with b.p. 77.0-78.0° and consisting of a constant boiling mixture of ethyl alcohol and 35% acetal. Thus, 26.6 g (24%) of the acetal had not entered into reaction, and the yield of ether is 68.8% of theory, calculated on the reacted acetal.

° Vinyl heptyl ether contains 99.5% pure substance.

Physical Properties of Vinyl Alkyl Ethers

Ether	Yield %	b.p. at 760 mm ±0.05°	d_4^{20} ±0.002 g/ml	n_C^{20} ±0.0001	n_D^{20} ±0.0001	n_F^{20} ±0.0001	γ^{20} ± 0.05 (dynes/cm)	MR_C Found	MR_C Computed	MR_D Found	MR_D Computed	MR_F Found	MR_F Computed	P Found	P Computed
$CH_2 = CHOC_2H_5$	50.3	35.72	0.7531	1.37396	1.37657	1.38280	19.00	21.863	21.713	21.999	21.848	22.324	22.145	199.7	199.8
$CH_2 = CHOC_3H_7$ (iso)	56.1	55.60	0.7534	1.38218	1.38475	1.3908	18.72	26.616	26.311	26.775	26.466	27.160	26.813	237.8	237.9
$CH_2 = CHOC_3H_7$	60.5	65.00	0.7674	1.38830	1.39084	1.39706	20.02	26.502	26.311	26.656	26.466	27.032	26.813	239.0	239.0
$CH_2 = CHOC_4H_9$ (iso)	60.0	82.98	0.7683	1.39398	1.39656	1.40263	20.54	31.191	30.909	31.362	31.084	31.788	31.481	277.5	276.8
$CH_2 = CHOC_4H_9$***	65.0	93.82	0.7792	1.39910	1.40166	1.40787	21.99	31.099	30.909	31.274	31.084	31.701	31.481	278.4	279.0
$CH_2 = CHOC_5H_{11}$ (iso)	60.5	112.5°	0.7826	1.40471	1.40721	1.41336	22.48	35.738	35.507	35.932	35.702	36.409	36.149	317.7	316.8
$CH_2 = CHOC_7H_{15}$	58.0	169.3 - 169.6°	0.8021	1.41948	1.42200	1.42808	25.45	44.825	44.703	45.062	44.938	45.629	45.485	398.3	399.1
$CH_3CH = CHOC_2H_5$****	53.7	69.1 - 69.4°	0.7754	1.39594	1.39662	1.40520	21.44**	26.686	26.311	26.846	26.466	27.226	26.813	239.0	239.0
$C_2H_5CH = CHOC_2H_5$****	68.3	94.9 - 95.3°	0.7761	1.40356	1.40627	1.41299	22.09**	31.531	30.909	31.718	31.084	32.179	31.481	279.8	279.0
$(CH_3)_2C = CHOC_2H_5$	74.0	94.02	0.7757	1.40426	1.40528	1.41277	21.62**	31.596	30.909	31.666	31.084	32.181	31.481	278.4	278.8
								30.909		31.084		31.481		30.909	

* ±0.10°.
** ±0.1 dynes/cm.
*** Supersonic velocity in vinyl butyl ether at 20° is 1140 m/sec.
**** Apparently a mixture of cis- and trans-isomers.

Vinyl isoamyl ether. 101.3 g (0.5 mole) diisoamylacetal was distilled over 1.5 g aniline sulfate. At 112-121°, 93.2 g of condensate distilled over. Fractional distillation (764 mm) gave 50.1 g of a fraction with b.p. 110-113° (vinyl-isoamyl ether containing about 10% isoamyl alcohol; ether yield 76%) and 34.8 g of a fraction with b.p. 129-131° (isoamyl alcohol; yield 78%). In the distillation flask was a residue of 6.5 g diisoamylacetal. After purification the first fraction yielded 34.5 g vinylisoamyl ether with b.p. 111.4° (743.2 mm) or 60.5% of theory.

β,β-Dimethylvinylethyl ether. 84 g (0.6 mole) diethylacetal of isobutyric aldehyde was distilled over 1.5 g of sulfanilic acid. 81.6 g distillate came over at 76.5-91.5°. It was washed four times with water, dried over potassium carbonate and sodium and distilled. Yield of pure substance with b.p. 93.9° (754 mm) 44.5 g, or 74% of theory.

SUMMARY

A method was developed for the synthesis of vinyl alkyl ethers by the catalytic cleavage of alcohols from acetals with the aid of sodium bisulfate, aniline sulfate, or sulfanilic acid. Ten vinyl alkyl ethers were prepared by this method and their physical properties are described.

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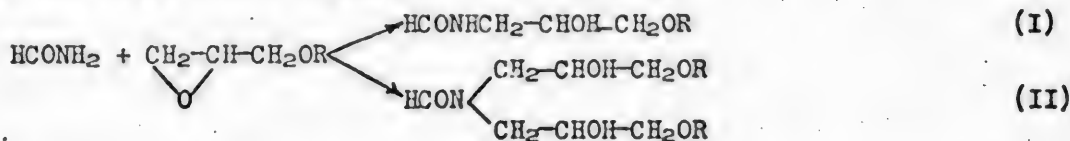# REACTION OF GLYCIDE AND ITS ETHERS WITH ACID AMIDES

II. REACTION OF GLYCIDE ETHERS WITH FORMAMIDE

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In the previous communication [1] one of us had shown that reaction of glycide with acetamide leads to formation of the mono- and dialkylolamides: N-propanediol-2,3-acetamide and N,N-di(propanediol-2,3)-acetamide. Continuing our studies in this direction, we have investigated the reaction of the methyl and ethyl ethers of glycide with formamide. No information on this reaction has appeared in the literature. Theoretically, formamide can react with glycide ethers both at the amido and the aldehyde group. It is more probable, however, that the ethers will react preferentially with the amido group owing to the greater mobility of the hydrogen atoms of the latter in comparison with the hydrogen atom of the aldehyde group.

The following products should be expected as a result of the reaction of the methyl and ethyl ethers of glycide with formamide:

$$HCONH_2 + CH_2-CH-CH_2OR \diagdown \qquad HCONHCH_2-CHOH-CH_2OR \qquad (I)$$

$$HCON \diagup \begin{matrix} CH_2-CHOH-CH_2OR \\ CH_2-CHOH-CH_2OR \end{matrix} \qquad (II)$$

where R is methyl or ethyl.

Experiments have shown that in all cases compounds with the formulas (I) and (II) are actually formed. It should be noted that other possible isomers with primary alcohol groups are apparently not formed. Or if they are formed, their amounts could not be determined when working with quantities of materials of the order of a few grams.

The reaction between glycide ethers and formamide was studied with material ratios of 1:1 and 1:2 under various conditions: at room and higher temperatures, and in the presence and absence of toluene. Under ordinary conditions the substances did not react even after a long time (3 months). Experiments were therefor performed with heating on an oil bath at 140° for 10 hours, and it was then found that glycide ethers react with formamide both in the 1:1 ratio and when the ether is in excess (2 moles) with formation simultaneously of mono- and disubstituted formamide. The mean yield of N-monosubstituted formamide was 30-33%, that of N,N-disubstituted formamide was 20-23%, and that of polymer was 23%. With rising temperature the yield of reaction products falls and more polymer is obtained.

The synthesized compounds are colorless liquids with characteristic and rather penetrating odors and a bitter taste. Their constants are listed in Table 1.

EXPERIMENTAL

1. Characteristics of the starting materials. The methyl and ethyl ethers

TABLE 1

Substance	Boiling point (5 mm)	d_4^{15}	n_D^{15}	MR Computed	MR Found
HCONH–CH$_2$CHOH–CH$_2$OCH$_3$	105-110	-1.1733	1.4502	32.07	30.40
HCONH–CH$_2$–CHOH–CH$_2$OC$_2$H$_5$	115-120	1.1102	1.4389	36.69	34.68
HCON(CH$_2$–CHOH–CH$_2$OCH$_3$)$_2$	190-195	1.1607	1.4655	55.05	52.58
HCON(CH$_2$–CHOH–CH$_2$OC$_2$H$_5$)$_2$ ...	200-205	1.1016	1.4558	63.29	61.48

of glycide were prepared from the corresponding ethers of monochlorhydrin, which in turn were prepared by chlorination of glycerol and removal of HCl from the α,γ-dichlorhydrin. Anhydrous glycerol in presence of glacial acetic acid as catalyst was saturated with gaseous HCl until the weight increase was 20% in excess of the theoretical requirement; the resultant α,γ-dichlorhydrin (yield 60%) was purified by distillation in vacuum [2] before heating at 60-65° and treating with the calculated amount of 10% caustic alkali heated to the same temperature, [3]. The epichlorhydrin of glycerol was generally obtained in a yield of 70-75%. Analysis by Stepanov's method gave chlorine 38.41% against the theoretical value of 38.32%. It had the constants: b.p. 115-118°, d_4^{15} 1.186; n_D^{15} 1.437; MR 20.43.

The corresponding ethers of glycerol monochlorhydrin were obtained by heating the epichlorhydrin with absolute methyl or ethyl alcohol in presence of sulfuric acid (sp. gr. 1.84) at 90-95° for 10-15 hours. The methyl ether (chloromethylin) was obtained in 40% yield, and the ethyl ether (chlorethylin) in 36.5% yield. Attention is drawn to the fact that if the amount of sulfuric acid is 2-3 times smaller than is recommended in the literature [4], the yield is increased to 65% for the methyl ether and to 55% for the ethyl ether.

The products obtained are oily liquids, soluble in alcohol and ether and with poor solubility in water. The constants of the chloroethers are listed in Table 2.

TABLE 2

| Substance	Boiling point	d_4^{15}	n_D^{15}	MR Computed	MR Found
CH$_2$Cl–CHOH–CH$_2$OCH$_3$	169-173	1.1687	1.4446	28.71	28.44
CH$_2$Cl–CHOH–CH$_2$OC$_2$H$_5$	185-189	1.1247	1.4450	33.32	32.76

Treatment of these chloroethers with concentrated caustic alkali yielded the methyl [5] and ethyl [6] ethers of glycide, but in yields of only 17-20%. Considerably improved results were obtained if the removal of HCl was effected by means of solid alkali in absolute ether by the method described in connection with the preparation of the epichlorhydrin [7]. The yield of methyl ether of glycide is then 41% and that of ethyl ether 54%.

Other methods of preparation of the methyl and ethyl ether of glycide are also described in the literature [8, 9, 10].

In Table 3 are given the constants of the glycide ethers prepared here and the corresponding literature data.

The ethers obtained were readily mobile liquids with pleasant odors, readily soluble in alcohol and ether and in 4-5 times the volume of water. Chemically, the methyl and ethyl ethers of glycide exhibit all the properties of α-oxides [9]. Recently the ethyl ether has begun to find practical application and is used as a new solvent for cellulose acetate and nitrocellulose, [12].

TABLE 3

Substance	Boiling point	d_4	n_D	MR Computed	MR Found
CH_2–CH–CH_2–O–CH_3	110-112°	0.9949	1.4040 at 15°	21.76	21.57
Literature data	115-118	–	–	–	[9]
	110.5	0.9877	1.4070 at 15°	21.78	22.94[11]
CH_2–CH–CH_2–O–C_2H_5 ...	128-130	0.9554	1.4080 at 15°	26.38	26.34
Literature data	128-129	0.9400	at 12°		[9]

2. Reaction of glycide methyl ether with formamide. The formamide had the constants: b.p. 110-112° at 12 mm; d_4^{15} 1.1461; n_D^{15} 1.445; MR_D 10.44 (computed 10.25). Nitrogen (Kjeldahl) 30.1% (31.11% computed).

5.2 g formamide and 10 g methyl ether of glycide were refluxed in a flask on an oil bath for 10 hours at 140°. The temperature in the flask was observed to rise from 105 to 130°. At the conclusion of heating the reaction product was fractionated in vacuum to yield 6 g (40%) N-propanol-2-methoxy-3-formamide, 3.4 g (27%) N,N-di-(propanol-2-methoxy-3)-formamide, and 2.8 g (17%) viscous polymer.

The identical products were isolated on heating 2.7 g formamide with 8 g (double excess) of the ether: 3.5 g (28.8%) N-propanol-2-methoxy-3-formamide, 2.5 g (19%) N,N-di-propanol-2-methoxy-3-formamide, and 2 g polymer.

Experiments conducted in presence of toluene with the aim of reducing the yield of polymer were unsuccessful. The products are colorless liquids readily soluble in water and in alcohol, benzene, or acetone. They gradually turn yellow on storage.

Analysis of N-propanol-2-methoxy-3-formamide:

0.1568 g substance: 12.48 ml 0.1 $\underline{N}$ H_2SO_4 (Kjeldahl).
0.1602 g substance: 12.69 ml 0.1 $\underline{N}$ H_2SO_4.
0.1258 g substance: 0.2301 g AgI (Zeisel).
Found %: N 11.14, 11.09; CH_3O 24.13.
$C_5H_{11}O_3N$. Computed %: N 10.52; CH_3O 23.31.

Determination of the number of hydroxyl groups. A weighed amount of substance was heated for 2 hours on the boiling water bath with a titrated mixture of acetic anhydride and pyridine (10% solution). After pouring into water, the excess of acetic acid was neutralized with 0.1 $\underline{N}$ caustic alkali solution.

0.1454 g substance: 10.99 ml 0.1 $\underline{N}$ NaOH.
0.1380 g substance: 10.46 ml 0.1 $\underline{N}$ NaOH.
Found %: OH 12.88, 12.87.
$C_5H_{10}O_2N(OH)$. Computed %: OH 12.78.

Analysis of N,N-di-(propanol-2-methoxy-3)-formamide:

0.1364 g substance: 6.49 ml 0.1 $\underline{N}$ H_2SO_4 (Kjeldahl).
0.1794 g substance: 8.42 ml 0.1 $\underline{N}$ H_2SO_4.
0.1896 g substance: 0.3752 g AgI (Zeisel).
Found %: N 6.66, 6.57; CH_3O 26.10.
$C_9H_{19}O_5N$. Computed %: N 6.33; CH_3O 28.06.

Determination of number of hydroxyl groups·

<div style="text-align:center">

0.2311 g substance: 20.53 ml 0.1 $\underline{N}$ NaOH.

0.1616 g substance· 14.51 ml 0.1 $\underline{N}$ NaOH.

Found %: OH 15.10, 15.26.

$C_9H_{17}O_3N(OH)_2$. Computed %: OH 15.38.

</div>

The polymer is a viscous oil with a more or less dark-red color. It is readily soluble in water, alcohol, benzene, ethylene dichloride, acetone, and carbon tetrachloride. At 210° (5 mm) it decomposes violently with evolution of copious vapors.

Analysis of the polymer:

<div style="text-align:center">

0.1515 g substance: 4.9 ml 0.1 N H_2SO_4 (Kjeldahl)

0.1642 g substance: 5.43 ml 0.1 N H_2SO_4.

Found %: N 4.52, 4.68.

</div>

3. Reaction of glycide ethyl ether with formamide.· From 7.7 g glycide ethyl ether and 2.3 g formamide were obtained, under the above-described conditions, 3 g (30%) N-propanol-2-ethoxy-3-formamide, 2.5 g (25%) N,N-di-(propanol-2-ethoxy-3)-formamide, and 2.5 g (25%) polymer.

The same products were obtained on heating 1.3 g formamide with 9.2 g (double excess) of the ethyl ether: 2.7 g (25.4%) N-propanol-2-ethoxy-3-formamide, 1.8 g (11.6%) N,N-di-(propanol-2-ethoxy 3-)formamide, and 4 g polymer.

It should be noted that similar results were obtained when the reaction was carried out in presence of toluene.

The products were colorless liquids which turned yellow when kept and had a characteristic odor and bitter taste. Readily soluble in water and organic solvents (alcohol, benzene, ether).

Analysis of N-propanol-2-ethoxy-3-formamide:

<div style="text-align:center">

0.1332 g substance: 8.9 ml 0.1 $\underline{N}$ H_2SO_4 (Kjeldahl).

0.1234 g substance· 8.35 ml 0.1 N H_2SO_4.

0.1898 g substance: 0.2956 AgI (Zeisel).

Found %: N 9.44, 9.50; C_2H_5O 29.82.

$C_6H_{13}O_3N$. Computed %: N 9.52; C_2H_5O 30.61.

</div>

Determination of number of hydroxyl groups:

<div style="text-align:center">

0.1534 g substance: 9.6 ml 0.1 $\underline{N}$ NaOH.

0.2122 g substance: 13.6 ml 0.1 $\underline{N}$ NaOH.

Found %: OH 10.63, 10.70.

$C_6H_{12}O_2N(OH)$. Computed %: OH 11.56.

</div>

Analysis of N,N-di-(propanol-2-ethoxy-3)-formamide:

<div style="text-align:center">

0.1304 g substance: 5.61 ml 0.1 N H_2SO_4 (Kjeldahl).

0.1820 g substance: 6.80 ml 0.1 $\underline{N}$ H_2SO_4.

0.1434 g substance: 0.2620 g AgI (Zeisel).

Found %: N 5.94, 5.95; C_2H_5O 35.09.

$C_{11}H_{23}O_5$. Computed %: N 5.62; C_2H_5O 36.15.

</div>

Determination of number of hydroxyl groups:

<div style="text-align:center">

0.1398 g substance: 11.13 ml 0.1 $\underline{N}$ NaOH.

0.1294 g substance: 10.35 ml 0.1 $\underline{N}$ NaOH.

Found %: OH 13.53, 13.59.

$C_{11}H_{21}O_3N(OH)_2$. Computed %: OH 13.65.

</div>

SUMMARY

1. A study was made of the reaction of the methyl and ethyl ethers of glycide with formamide.

2. The following products of these reactions were prepared and characterized: N-propanol-2-methoxy-3-formamide; N,N-di-(propanol-2-methoxy-3)-formamide; N-propanol-2-ethoxy-3-formamide; and N,N-di-(propanol-2-ethoxy-3)-formamide.

3. It was shown that these products are obtained both when using a 1:1 ratio of components and when using an excess of the ether, i.e., a 1:2 ratio.

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SYNTHESES WITH ACRYLONITRILE

## XI. THE CYANOETHYLATION OF ETHYLENE DIAMINE

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Reaction of acrylonitrile with secondary amines leads to good yields of N-(β-cyanoethyl)-amines, i.e., N-substituted β-aminopropionitriles. A series of our preceding investigations was devoted to the study of this reaction [1,2]. Up to now the problem of the action of acrylonitrile upon primary amines, not to mention diamines, has not been investigated. In the latter case it would be important to establish the fate of the second cyanoethyl group. Qualitatively, it seemed more likely that the second amino group would be cyanoethylated, since there are indications in the literature that acrylonitrile enters more reluctantly into reaction with a singly cyanoethylated amino group [3].

We performed experiments with the simplest member of the diamines, namely, ethylene diamine. As had been expected by analogy with aliphatic monoamines, the reaction between acrylonitrile and ethylene diamine proceeds very energetically and with considerable evolution of heat. Reaction of 2 moles of acrylonitrile per mole of ethylene diamine yielded products of monocyanoethylation, dicyanoethylation, and (in minor quantity) of a more complex reaction, probably polycyanoethylation. The product of monocyanoethylation, i.e., N-(β-cyanoethyl)-ethylene diamine, was obtained in a yield of 39.8% of the theoretical; and the product of dicyanoethylation in a yield of 59.8% of the theoretical.

For the purpose of extablishing the structure of the product of dicyanoethylation of ethylene diamine, we used the method of determination of the active hydrogen with the aid of methyl zinc iodide, developed by Terentyev and Shor [4]. Methyl zinc iodide differs from methyl magnesium iodide in reacting quantitatively at room temperature with only one hydrogen atom of the primary amino group, and in giving a value of 0.1-0.2 hydrogen atom in reaction with secondary amines. Quantitative determination is effected at 100° of all of the hydrogen atoms, both those of the primary and those of the secondary amino group, while the α-labile hydrogen atoms of nitriles remain intact.

Two main structural formulas may be advanced for the product of dicyanoethylation of ethylene diamine:

$$CH_2-NH-CH_2CH_2CN$$
$$|$$
$$CH_2-NH-CH_2CH_2CN$$
(I)
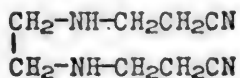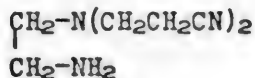
$$CH_2-N(CH_2CH_2CN)_2$$
$$|$$
$$CH_2-NH_2$$
(II)

The determination of the active hydrogen gave 0.31 hydrogen atom at room temperature and 1.94 atoms at 100°. Thus, the analytical data point to the presence in the molecule of two secondary amino groups, in agreement with formula (I).

We carried out the reaction with a 20% aqueous solution of ethylene diamine, with ethylene diamine monohydrate, and with anhydrous ethylene diamine. In presence of water the reaction is violent, but partial hydrolysis of the aminonitriles is observed with appreciable darkening of the reaction mixture.

After obtaining perfectly satisfactory results in the dicyanoethylation of ethylene diamine, we proceeded to the cyanoethylation of trimethylene diamine and tetramethylene diamine with the aim of developing a synthesis of spermine, spermidine, and their analogs. The constants of the compounds prepared have been published by one of the authors of the present paper [2]. While this paper was being prepared for the press, Schultz [5] published a short communication to the effect that he had prepared spermine by cyanoethylation of putrescine followed by reduction. He did not isolate any intermediate products. Our experiments in this field will be the subject of a later communication.

EXPERIMENTAL

Cyanoethylation of Ethylene Diamine

35 g (0.66 mole) dry acrylonitrile was added dropwise with energetic stirring and external cooling to 20 g (0.33 mole) anhydrous ethylene diamine dissolved in 50 ml of ether. The rate of addition of the acrylonitrile and the degree of cooling were so adjusted that the temperature of the mixture was maintained at 15 to 20°. If the temperature is too low the reaction does not take place, and if it is too high energetic self-heating occurs with darkening of the reaction mixture.

After the whole of the acrylonitrile has been added, which requires about 2 hours, the mixture is periodically stirred over a period of two hours, and left overnight in a tightly closed vessel at room temperature. The ether and traces of unreacted acrylonitrile are then distilled off and the residue fractionated in vacuum, giving 15.0 g of the product of monocyanoethylation (b.p. 100-103° at 1.5 mm) or 39.8% of the theoretical yield calculated upon the ethylene diamine, and 33.1 g of the product of dicyanoethylation (b.p. 170-176° at 1.5 mm), or 59.8% of theory. There was also obtained a small amount of dark-brown residue, readily soluble in water, distilling at 250-300 and 1.5 mm with much decomposition.

N-(β-Cyanoethyl)-ethylene diamine is obtained in the pure form by repeated vacuum distillation of the product of monocyanoethylation of ethylene diamine. It is a colorless and very viscous liquid, readily soluble in water and alcohol, and fuming in the air:

B.p. 101° at 1.5 mm: d_4^{20} 0.9912; n_D^{20} 1.4727; MR_D 32.19.
$C_5H_{11}N_3$. Computed: MR_D 32.2.

2.950 mg substance: 0.967 ml N_2 (24°, 742 mm).
Found %: N 36.78.
$C_5H_{11}N_3$. Computed %: N 37.15.

Determination of activation hydrogen by the method of Terentyev and Shor [4], using methyl zinc iodide.

a) At room temperature (determination of primary amino group):

0.0170 g substance: 4.2 ml CH_4 (26.6°, 720.1 mm).
Found: 1.08 active H atoms.

b) At 100° (determination of total number of active H atoms):

0.0170 g substance: 11.8 ml CH_4 (26.6°, 720.1 mm).
Found: 3.02 active H atoms.
$NH_2(CH_2)_2NH(CH_2)_2CN$. Computed: 3.0 active H atoms.

The picrate and styphnate separate from benzene as a yellow oil. The mono-benzoyl derivative is a colorless oil. The hydrochloride is extremely hygroscopic.

N,N'-Di-(β-cyanoethyl)-ethylene diamine is obtained by vacuum distillation of the product of dicyanoethylation of ethylene diamine. It is a thick, slightly opalescent oil, free from odor. It is highly soluble in water and alcohol, and poorly soluble in ether:

B.p. 174° at 1.5 mm; 191° at 3.5 mm; d_4^{20} 1.0256; n_D^{20} 1.4793; MR_D 45.97. $C_{18}H_{14}N_4$. Computed: MR_D 46.12.

4.200 mg substance: 1.250 ml N_2 (21°, 746 mm).
4.053 mg substance: 1.206 ml N_2 (23°, 745 mm).
Found %: N 33.92, 33.64.
$C_8H_{14}N_4$. Computed %: N 33.73.

The picrate and styphnate separate in the form of a non-crystallizing oil on precipitation from benzene. The hydrochloride comes down as needles from ether solution, and forms silky needles on recrystallization from aqueous methyl alcohol. M.p. 184-187° (with decomposition).

Determination of active hydrogen by the method of Terentyev and Shor [4], using methyl zinc iodide:

a) At room temperature:

0.0300 g substance: 1.50 ml CH_4 (21.1°, 731 mm).
Found: 0.31 active H atom.

b) At 100°:

0.0300 g substance: 8.90 ml CH_4 (21.1°, 730 mm).
Found: 1.94 active H atom.
$NC(CH_2)_2NH(CH_2)_2NH(CH_2)_2CN$. Computed: 2.0 active H atom.

SUMMARY

1. The products of mono- and dicyanoethylation resulting from the action of acrylonitrile on ethylene diamine have been prepared, isolated, and character-ized.

2. The product of dicyanoethylation of ethylene diamine is found to have a linear structure, i.e., it is N,N'-di-(β-cyanoethyl)-ethylene diamine.

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THE MECHANISM OF TRANSFORMATION

OF DIACETONE-2-KETO-l.GULONIC ACID INTO l-ASCORBIC ACID

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One of the most convenient methods for transforming diacetone-2-keto-l-gu-
lonic acid into l-ascorbic acid consists in heating it in a chloroform medium in
the presence of ethyl alcohol and hydrogen chloride [1,2,3]. However, the mech-
anism of this reaction, which proceeds in an almost anhydrous medium, is insuf-
ficiently clear. For conversion into l-ascorbic acid, the diacetone-2-keto-l-
gulonic acid must first be hydrolyzed with detachment of two acetone residues. It
is known that in an aqueous medium the hydrolysis proceeds with formation of 2-
keto-l-gulonic acid [4].

We have shown that under anhydrous conditions, in an indifferent solvent in
presence of alcohol and mineral acid, the heating of diacetone-2-keto-l-gulonic
acid for one hour converts it into the ester of 2-keto-l-gulonic acid. Conse-
quently, both hydrolysis and esterification occur simultaneously in this reaction,
the alcohol esterifying the carboxyl group. The acetone residues are split off
in the form of two molecules of acetone and not in the form of acetonyl chloride,
which should be formed if the fission was effected with participation of hydrogen
chloride. The water required for the formation of acetone originates from the
single molecule of water of crystallization present in the original diacetone-2-
keto-l-gulonic acid, while a second molecule of water is formed during esterifica-
tion.

This reaction may serve for the preparation of esters of keto-hexonic acids,
and in particular for the preparation with hydrogen chloride of the methyl ester
of 2-keto-l-gulonic acid, instead of the reaction with diazomethane [4].

Consequently, the first stage in the transformation of diacetone-2-keto-l-
gulonic acid is its hydrolysis and the formation of the ester of 2-keto-l-gulonic
acid.
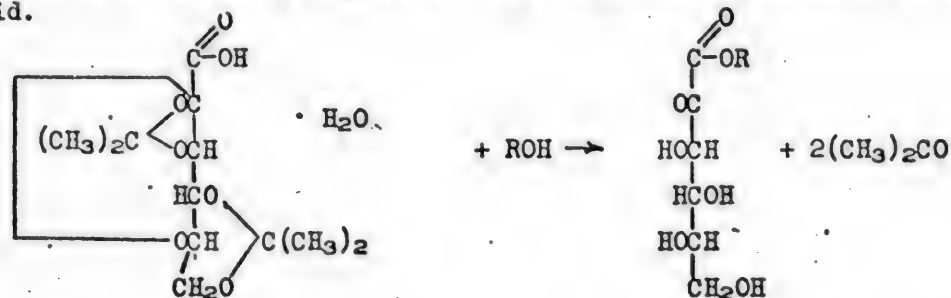
This step is absolutely essential for the formation of l-ascorbic acid. In
the second step the ester, in an indifferent solvent, is subjected to further

transformation under the influence of acids – both mineral and organic (although in the latter case the reaction velocity is considerably lower) – into l-ascorbic acid as a consequence of splitting-off of a molecule of alcohol from the ester of 2-keto-l-gulonic acid with concomitant keto-enol rearrangement and closing of the γ-lactone ring.

Diacetone-2-keto-l-gulonic acid would not be converted into l-ascorbic acid without passage through the ester stage, as is evident from the fact that in presence of organic acid it does not yield l-ascorbic acid, since the esterification reaction does not then take place and, consequently, the intermediate ester of 2-keto-l-gulonic acid cannot be formed.

The second stage of the reaction depends upon the character of the catalyst, the hydrogen ion concentration and the temperature. The velocity of the reaction in presence of hydrogen chloride is 3-4 times greater than that in the presence of sulfuric acid. A temperature rise of $10.7°$ causes a more than threefold increase in the reaction velocity. Experimental results are plotted in Fig. 1.
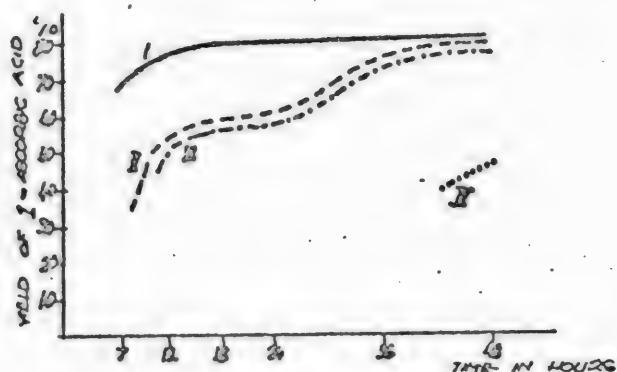
The product of transformation of diacetone-2-keto-l-gulonic acid consists almost entirely of the ester of 2-keto-l-gulonic acid and l-ascorbic acid. The composition of the reaction product after transformation via the methyl ester is plotted in Fig. 2 as a function of duration of the reaction.

Fig. 1. Yields of l-ascorbic acid.

I-with HCl at $70.6°$; II-with HCl at $59.9°$;
III-with H_2SO_4 at $70.6°$; IV-with H_2SO_4 at $59.9°$.

We found that higher alcohols can also be successfully used in preparing intermediate esters of 2-keto-l-gulonic acid. The velocity of transformation of diacetone-2-keto-l-gulonic acid with normal propyl and butyl alcohols, as well as with isobutyl alcohol, is not significantly different from that with ethyl alcohol, but a slowing-down occurs with isoamyl alcohol. When using higher alcohols the yield of l-ascorbic acid likewise depends upon the catalytic participation of water; results are shown in the table.

Transformation of Diacetone-2-keto-l-gulonic Acid in Ethylene Dichloride Medium in Presence of Hydrogen Chloride and Absolute Alcohol After 18 Hours at the Boiling Pt. of the Azeotropic Mixture

Alcohol	Per cent yield of l-ascorbic acid	
	In absence of water	Under catalytic influence of 0.3 mole water
Methyl	73	73
Ethyl	78	82
n-Propyl	67-78	81.8
n-Butyl	60-70	81.5
Isobutyl	59-68	82
Isoamyl	57-68	77.5

The transformation of diacetone-2-keto-1-gulonic acid into 1-ascorbic acid may be effected not only in chloroform [1], but also in other inert solvents: in aromatic hydrocarbons, halo-substituted aliphatic and aromatic hydrocarbons, in decahydronaphthalene, etc. at the boiling points of their azeotropic mixtures [5].

Fig. 2. Composition of the products of transformation of diacetone-2-keto-1-gulonic acid into 1-ascorbic acid via the methyl ester. Iodine and alkali titration curves are combined.

EXPERIMENTAL

Methyl Ester of 2-Keto-1-gulonic Acid

20 g of diacetone-2-keto-1-gulonic acid containing one molecule of water of crystallization, 40 ml of ethylene dichloride, and 15 ml of 7% solution of hydrogen chloride in dry methyl alcohol were heated on a water bath (65°) under a reflux condenser with stirring for one hour. A precipitate begins to separate out after 40-45 minutes. On the following day the precipitate is filtered off, and washed first with ethylene dichloride and then with a mixture of ethylene dichloride and alcohol (4:1). There is obtained 11.7 g (82%) of the methyl ester of 2-keto-1-gulonic acid, m.p. 153-155°. For analytical purposes the substance was recrystallized from methyl alcohol and melted at 156-157°.

4.220 mg substance: 6.197 mg CO_2; 2.325 mg H_2O.
3.570 mg substance: 5.217 mg CO_2; 1.980 mg H_2O.
Found %: C 40.07, 39.88; H 6.16, 6.20.
$C_7H_{12}O_7$. Computed %: C 40.36; H 5.82.

1-Ascorbic Acid

a) Experiments were carried out in the following manner for determination of the composition of the reaction products.

20 g of crystalline diacetone-2-keto-1-gulonic acid, 45 ml ethylene dichloride and 9 ml dry methyl alcohol containing 18% hydrogen chloride were refluxed on a water bath at 70° with stirring. The separated product was filtered off, washed and dried, and analyzed for ascorbic acid content and total acidity. In experiments in which heating was continued only for a short time, the methyl ester of 2-keto-1-gulonic acid was isolated in the pure state, m.p. 156-157°.

b) The following procedure was applied in order to determine the influence of various factors upon the velocity of transformation of diacetone-2-keto-1-gulonic acid into 1-ascorbic acid.

20 g diacetone-2-keto-1-gulonic acid (containing 93.8% anhydrous acid), 45 ml inert solvent (chloroform or ethylene dichloride) and 9 ml 96% ethyl alcohol containing 18% hydrogen chloride, or a mixture of 7.5 ml of 96% ethyl alcohol and 1.5 g concentrated sulfuric acid were refluxed on a water bath with vigorous stirring. Reaction was effected at the boiling temperature of the azeotropic mixture: with chloroform at 59.4-59.9°, and with ethylene dichloride at 70.1-70.6°. After cooling, the 1-ascorbic acid was filtered off, washed with the solvent (chloroform or ethylene dichloride) and then with a mixture of alcohol and solvent (1:4).

The optimum conditions for the reaction are: heating at the boiling point
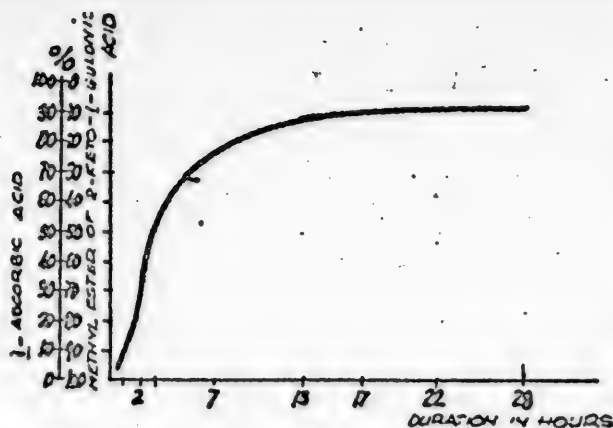
of the azeotropic mixture for 13 hours of a mixture of 20 g diacetone-2-keto-1-gulonic acid (crystalline), 40 ml ethylene dichloride, and 6 ml of 96% ethyl alcohol containing 18% hydrogen chloride. Yield 9.8-9.9 g (81-82%) of 1-ascorbic acid with a content of 98-99% by the iodine method.

c) Determination of acetone.

About 80 ml liquid was distilled off from the reaction mixture while stirring (ethylene dichloride was added to the flask to make up for loss in course of distillation). This distillate was repeatedly extracted with water. In the aqueous extract acetone was determined by conversion to iodoform with caustic alkali solution and iodine. 28.1 g iodoform with m.p. 119° was obtained. 52% of the theoretically possible amount of acetone was thus accounted for.

SUMMARY

1. The transformation of diacetone-2-keto-1-gulonic acid into 1-ascorbic acid proceeds by the following mechanism: under the influence of mineral acids and in presence of an anhydrous inert solvent and an alcohol, the crystalline acid first undergoes hydrolysis with concomitant esterification of the carboxyl group of 2-keto-1-gulonic acid; subsequently the latter compound splits off the alcohol with cyclization of the molecule to form the γ-lactone, and with keto-enol rearrangement to 1-ascorbic acid.

2. A simple method has been developed for the preparation of esters of keto-hexonic acids.

3. The transformation of diacetone-2-keto-1-gulonic acid into 1-ascorbic acid was studied in dependence on the experimental conditions.

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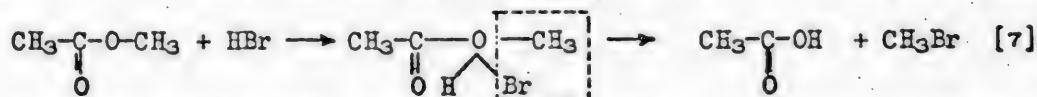
SAPONIFICATION OF ESTERS OF ORGANIC ACIDS

I. SAPONIFICATION OF ESTERS OF MONOCARBOXYLIC ACIDS

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Previous authors have studied the processes of hydrolysis and saponification of esters of organic acids [1,2]. The mechanism of these reactions may be considered to have been established by the work of N.A.Menshutkin [3], B.V.Tronov [4], and Ch. Prevost [5]. The latter studies indicate that during hydrolysis and saponification of esters the bond between the oxygen of the alcohol radical and the carbon atom of the carboxyl group is ruptured. A similar conclusion about the fate of this bond was reached in a study of the hydrolysis of esters by water containing heavy oxygen [6].

In the cleavage of esters of organic acids by hydrogen halides, the bond between the alcohol radical and oxygen is ruptured according to the scheme:

$$CH_3-\underset{O}{\overset{\parallel}{C}}-O-CH_3 + HBr \longrightarrow CH_3-\underset{O\ \ H}{\overset{\parallel}{C}}-O-CH_3\ Br \longrightarrow CH_3-\underset{O}{\overset{\parallel}{C}}-OH + CH_3Br \quad [7]$$

B.V.Tronov and his co-workers arrive at the following conclusions in a study of the cleavage of esters by hydrogen bromide solutions [8].

1. Hydrocarbon radicals can be arranged in the following order in respect to the velocity of rupture of the bond with oxygen:

$$C_6H_5CH_2 > CH_3 > C_2H_5 > C_5H_{11} > C_6H_5.$$
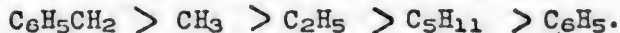
2. Acids may be arranged in the following order in respect of the velocity of decomposition of HBr of their esters containing the same hydrocarbon radicals:

$$HCOOH > CH_3CH_2COOH > CH_3COOH > C_6H_5COOH > CH_2ClCOOH.$$

The objective of the present investigation was to determine the relative velocity of the saponification of esters of monocarboxylic acids by caustic alkali solution in order to establish the dependence of the saponification velocity on the degree of dissociation of the acids. Another objective was to compare the velocity of this reaction with the velocity of cleavage of esters by hydrogen bromide.

We made a study of triacetin in view of the publication of a paper on the action of aluminum chloride on esters of polyhydric alcohols [9].

EXPERIMENTAL

Esters used in the investigation were: 1) methyl benzoate, 2) ethyl benzoate, 3) ethyl acetate, 4) butyl acetate, 5) amyl acetate, 6) ethyl formate,

7) ethyl isobutyrate, 8) glyceryl acetate (triacetin).

These compounds were carefully purified by distillation. Saponification was effected with aqueous alcoholic (60% alcohol) solutions of NaOH of concentration of 0.4 $\underline{N}$ (with a precise titer). Some of the esters were saponified too rapidly by alkali of this concentration, and in those cases a solution of 0.18 $\underline{N}$ concentration was used. To an exact amount of the ester in a small flask was added 25 ml of the alkali solution (1.5-2-fold excess of alkali), the mixture gently and uniformly agitated, and then allowed to stand for definite periods (15 min., 30 min., etc.) at 17-18°.

After a definite period of time, 25 ml of distilled water was added to the reaction mixture to slow down the saponification, and titration was performed with a weak solution of acetic acid to determine the residual alkali in the mixture. The percent saponification could then be calculated after a definite interval of time.

Three esters were saponified with an aqueous solution of NaOH, and the remainder were saponified unequally in aqueous solution owing to poor solubility.

TABLE 1

Formula of ester	Aqueous alcoholic solution of NaOH, 0.4 N			Aqueous solution of NaOH, 0.4 N		
	Duration of saponification (min).	Percent saponification	K	Duration of saponification, min.	Percent saponification	K
$C_6H_5COOC_2H_5$ .... {	15	26.34	0.023	15	9.40	0.0078
	30	38.49	0.021	30	18.94	0.0078
	60	53.10	0.019	60	31.85	0.0076
	Mean K =		0.021			
$C_6H_5COOCH_3$ ..... {	15	36.91	0.039	15	38.57	0.042
	30	48.24	0.031	30	58.18	0.046
	60	65.40	0.031	60	71.23	0.041
	Mean K =		0.034			
$(CH_3)_2CHCOOC_2H_5$ {	15	46.70	0.058	–	–	–
	30	61.85	0.054	–	–	–
	60	79.0	0.062	–	–	–
	Mean K =		0.058			
$CH_3COOC_5H_{11}$ .... {	15	83.78	0.344	15	51.68	0.071
				30	74.65	0.098

A more accurate comparison of the velocity of saponification was obtained by calculation of the velocity constant for a bimolecular reaction.

The experimental results are listed in Table 1 and 2.

By comparing the velocity constants of saponification, taking as unity the constant for ethyl isobutyrate, we obtain the relative values listed in Table 3.

TABLE 2

Name of ester		Duration of saponifica- tion (min).	Per cent saponifi- cation	K
Aqueous alcoholic solution of NaOH, 0.18 N				
Ethyl acetate	{	10	69.0	0.223
		20	81.5	0.220
		40	89.8	0.223
			Mean K =	0.222
Butyl acetate	{	10	74.2	0.288
		20	82.4	0.231
		40	89.3	0.209
			Mean K =	0.243
Amyl acetate	{	10	49.2	0.097
		20	63.15	0.085
		40	72.25	0.065
			Mean K =	0.082
Ethyl isobutyrate	{	10	20.3	0.027
		20	41.3	0.035
		40	56.4	0.032
			Mean K =	0.031
Glyceryl acetate	{	10	78.8	0.371
		20	87.8	0.360
		40	92.6	0.312
			Mean K =	0.348
Ethyl formate	{	5	96.2	--

We see from the data of Table 3 that esters of acetic acid are saponified very readily by weak alkali solutions; ethyl and butyl esters are saponified with nearly the same velocities, and amyl esters two to three times more slowly.

Ethyl acetate is saponified 7 times more rapidly than ethyl isobutyrate and 18 times more rapidly that ethyl benzoate.

TABLE 3

Name of compound	Relative velocity of saponification
Ethyl isobutyrate ..	1
Amyl acetate........	2.7
Ethyl acetate.......	7.1
Butyl acetate.......	8.0
Glyceryl acetate....	11.2
Methyl benzoate	0.63
Ethyl benzoate	0.40

The sequence of the changes in the velocity of saponification of esters is comparable with that in their hydrolysis by hydrogen bromide [8].

The acetate of a trihydric alcohol (glycerol) is saponified 1.5 times more rapidly than ethyl acetate; the saponification also proceeds rapidly to a conclusion.

Under our conditions ethyl formate was saponified very quickly.

SUMMARY

1. A study was made of the velocity of saponification of esters of formic, acetic, isobutyric, and benzoic acids.

Per acidic group K - 0.110.

2151

2. It was established that esters of acetic acid (a weak acid) are saponified more rapidly than those of the stronger benzoic acid, but the ethyl ester of formic acid (a relatively strong acid) is saponified with great ease; this is probably bound up with the special structure of formic acid.

3. The changes in the velocity of saponification of the esters of the investigated acids by aqueous alcoholic solutions of caustic alkali exhibit the same regularity as in their hydrolysis by hydrogen bromide.

4. In aqueous alkali solution the saponification takes place with a lower velocity than in aqueous alcoholic solution, but in the same order of relative velocities.

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HIGH-MOLECULAR COMPOUNDS

XXVI. POLYMERIZATION OF VINYL IODIDE AND SOME PROPERTIES OF 1,2-DIIODOETHANE [1]

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As we have previously shown [2], stereochemical factors play an important part in the processes of polymerization of unsaturated compounds. A principal factor is the size of the substituents on the carbon atoms linked by a double bond. If the volume of these substituents is sufficiently large, and if their number is large (not less than two), then steric hindrance is developed, and the compound is incapable of polymerization, or at the best it forms a dimer. That this phenomenon is undoubtedly bound up with the size of the substituents can be seen from Table 1, which gives the dimensions of substituents [3] and indicates the polymerizing ability of the corresponding substituted ethylenes [2] (a plus sign denotes polymerizing ability, a minus sign the absence thereof).

TABLE 1

Substituent	Radius of substituent (in Å)		Polymerizing ability in presence of ethylene				
	Internal	External	Of one substituent	Of two substituents in 1,1-position	Of two substituents in the 1,2 position	Of three substituents	Of four substituents
H	0.32	1.2				+	+
F	0.72	1.4	+	+	+	+	+
Cl	0.99	1.7	+	+	-(dimer)	- (dimer)	-
CH_3	1.09	1.9	+	+	-(dimer)	- (dimer)	-
Br	1.14	1.9	+	+	-	-	-
I	1.33	2.1	?	?	-	-	-
C_6H_5	2.32	3.1	+	-(dimer)	-(dimer)	-	-

As we see from Table 1, the only doubtful cases are the mono- and di-iodoethylenes. It is well known that all the representatives of this group of compounds of the type of $CH_2=CHX$ and $CH_2=CX_2$ containing fluorine, chlorine, or bromine, are readily polymerized. This was demonstrated in the investigations of Lvov [4], Kucherov [5], Ostromyslensky [6], and others [7]. Vinyl iodide, in contrast to its analogs, has not been obtained in the polymeric form although attempts to do so have been made. Thus, Baumann [8] unsuccessfully attempted to polymerize vinyl iodide while irradiating it with sunlight. Spence [9] has described the preparation of vinyl iodide from 1,2-diiodoethane and pointed out that

it is extremely stable and incapable of polymerization. It might be possible, however, to explain these failures by the fact that vinyl iodide, like all iodides, may not be very stable and might easily lose iodine. The latter is, of course, a strong inhibitor and suppresses the polymerization of many vinyl compounds, as was shown by Krakau [10] in respect of styrene, by Kucherov [5] in respect of vinyl bromide, and by other authors [8].

With the aim of clarifying the polymerizing ability of vinyl iodide, the present investigation was undertaken. Vinyl iodide was prepared from 1,2-diiodoethane by treatment with an alcoholic solution of sodium alcoholate. The 1,2-diiodoethane was synthesized and subjected to more detailed examination.

1,2-Diiodoethane was prepared by Spence's method [9] by addition of iodine to ethylene in alcoholic solution; it forms brown crystals melting at 79°. Yield 45% of theory. 1,2-Diiodoethane proved to be a most unstable substance, readily breaking down to iodine and ethylene. This decomposition readily takes place under the action of an alcoholic solution of sodium hydroxide or sodium alcoholate. Intensive decomposition of 1,2-diiodoethane also takes place in the presence of ammonium thiocyanate or potassium iodide. The degree of decomposition depends on the nature of the reagent and its quantity and concentration, and on the nature of the solvent, as indicated in Table 2.

TABLE 2

Reagent	Medium	No. of moles reagent per mole diiodoethane	% concentration of solution of reagent	Per cent decomposition of diiodoethane
Ammonium thiocyanate	Alcohol	3.7	20	19.7
	Alcohol	5.5	20	31.6
	Alcohol	11.5	20	46.2
Potassium iodide	Alcohol	37.0	40	83.0
	Alcohol	4.22	10	36.0
	Acetone	0.047	0.8	63.0
Sodium hydroxide	Alcohol	2.0	9.0	79.25
Sodium ethylate	Alcohol	1.0	20.36	96.77

Decomposition proceeds intensively on heating to 30-40°. A gas was given off which was collected in a gasholder, and from its amount the per cent decomposition of diiodoethane was determined (last column of Table 2). The gas was identified as ethylene; it yielded 1,2-dibromoethane with bromine. 1,2-Diiodoethane consequently decomposes according to the equation:

$$ICH_2 - CH_2I \rightarrow I_2 + CH_2 = CH_2$$

The liberated iodine was combined with a suitable reagent, and clearly the intensity of this process governed the degree of decomposition of the diiodoethane. The looseness of the combination of iodine in 1,2-diiodoethane is demonstrated by the fact that even potassium iodide suffices for its cleavage and forms with it the extremely labile complex KI_3. Alcoholic solutions of an alcoholate or caustic alkali are naturally still more active since they bind iodine with formation of stable compounds such as iodoform. The ease with which 1,2-diiodoethane decomposes under the action of alkaline agents is evidently bound up with the ready polarizability of the atoms of iodine liberated at the instant of reaction.

Vinyl iodide was prepared by heating an alcoholic solution of sodium alcoholate with 1,2-diiodoethane. Spence, who described this method, pointed out that he was able to obtain a fairly high yield [9]. We failed, however, to obtain on any occasion a yield of vinyl iodide greater than 1-2% of theory. Formation of vinyl iodide is apparently accompanied by decomposition into ethylene and iodine. In this case the latter reaction predominates. We changed the reaction conditions and used sodium hydroxide in alcoholic solution, but the resultant yields were even lower. The best procedure proved to be the use of dilute solutions of sodium ethylate without heating. The reaction mixture was left at room temperature in a closed flask in the dark for a few days; the flask was shaken from time to time. By this method the yield of vinyl iodide was increased 2-3 times.

The first attempts to polymerize vinyl iodide ended in failure. No polymerization occurred on heating it in a sealed ampoule; nor on heating it with addition of benzoyl peroxide or diazoaminobenzene, nor in emulsion. On the hypothesis that the iodine evolved on decomposition of vinyl iodide hindered polymerization, we attempted to bind the iodine by including silver in the ampoule. But the silver soon became coated with a crust of silver iodide and no polymerization took place. Boron fluoride merely led to rapid decomposition of the vinyl iodide. Application of 0.1 N sodium hyposulfite as a medium for heating with benzoyl peroxide enabled polymerization to be effected. However, the amount of polymer that we obtained was very small so that we can only characterize it in broad outline. It is a dark, crumbly powder, completely soluble in cresol and partially soluble in ethylene dichloride and ethylene dibromide. It is insoluble in such solvents as nitrobenzene, carbon tetrachloride, benzene, acetone, and alcohol.

With the objective of obtaining conclusive evidence that iodine was indeed the cause of prevention of polymerization, we prepared vinyl bromide and carried out its polymerization in presence of iodine. Polymerization was actually found to be retarded on addition of iodine; in the presence of an appreciable amount of iodine the polymerization of vinyl bromide proceeds with great difficulty and only after a long period. The polymer of vinyl bromide obtained in presence of iodine was strongly colored, resembling in this respect the polymer of vinyl iodide. On the other hand, pure vinyl bromide polymerizes with great ease in presence of benzoyl peroxide. Polyvinyl bromide was subjected to saponification with caustic alkali in dioxan and was found to lose a large proportion of bromine. In this respect it resembled polyvinyl chloride [13]. Treatment with potassium iodide did not lead to removal of iodine, which confirms the structure of polyvinyl bromide as a 1,3-dibromo derivative [14].

EXPERIMENTAL

Preparation of 1,2-diiodoethane [9]. In three interconnected test-tubes, fitted with side tubes and bubbling tubes, were placed 500 g of iodine crystals wetted with 150 ml of 80% alcohol. A rapid stream of ethylene was passed through this slurry. The reaction vessels were irradiated with a 1000 watt lamp. The iodine crystals gradually disappeared as the ethylene was passed through, and fine acicular crystals with a yellow color were formed (dii..oethane). When the passage of ethylene was concluded, the contents of the tubes were washed free from iodine with a dilute aqueous solution of potassium iodide. The crystals of 1,2-diiodoethane were then washed several times with water, drained on the filter, and dried in a desiccator. The melting point of the crude product was 79°. From 500 g iodine were usually obtained 230-250 g 1,2-diiodoethane.

Decomposition of 1,2-diiodoethane with caustic alkali. To 140 g 1,2-diiodoethane was added a solution of 40 g sodium hydroxide in 350 ml ethyl alcohol. The flask was heated on the water bath. 10.62 liters of gas containing 87% ethylene

was given off; the per cent decomposition was therefore 80%. A thick, dark oil and iodoform remained in the flask.

Decomposition of 1,2-diiodoethane with potassium iodide. To 11.5 g of 1,2-diiodoethane was added 40 ml of 0.6% solution of potassium iodide in acetone. The flask was gently heated on the water bath. Gas began to come off at a temperature of 25-30°. 0.58 liter of ethylene, corresponding to 63% decomposition, was evolved. Treatment with an alcoholic solution of potassium iodide resulted in only 36% decomposition, probably owing to the lower solubility of 1,2-diiodoethane in alcohol.

Decomposition of 1,2-diiodoethane with ammonium thiocyanate. Reaction begins on heating to 23°. The reaction proceeds very violently at a temperature of the order of 45-48°. The experimental results are shown in Table 2.

Preparation of vinyl iodide [9]. Into a two-necked flask equipped with a dropping funnel, connected to a reflux condenser, and placed on the water bath was introduced 150 g diiodoethane. Addition was slowly made from the dropping funnel of 178 ml of 3 N solution of sodium alcoholate. Copious evolution of gas was observed during the addition of the ethylate; the gas was passed through the water-cooled vertical condenser and a worm condenser cooled to −30 to −50° before entering the gasholder. When all of the sodium ethylate has been added, the flask was slowly heated on the water bath. The liquid collecting in the receiver was diluted with cold salt water when a yellow oil settled to the bottom of the receiver; it was separated from the water, dried over calcium chloride, and distilled. The main fraction boiled at 56° and consisted of vinyl iodide. Yield 1-1.5 g.

Decomposition of 150 g 1,2-diiodoethane with 178 ml of 3 N sodium alcoholate solution was accompanied by evolution of 14.5 liters of gas containing 81.6% ethylene.

Polymerization of vinyl iodide. 0.7 g vinyl iodide and 1.5 ml 0.1 N sodium hyposulfite solution were placed in an ampulla. The ampulla was sealed, placed in a drying cupboard kept at a temperature of 150°, and periodically shaken. After a little time the vinyl iodide was converted into a dark friable mass. The product was completely soluble in cresol and partly soluble in ethylene dichloride and ethylene dibromide.

Preparation of vinyl bromide [s]. 130 g potassium hydroxide, 250 ml water, 150 g ethylene dibromide, and 500 ml ethyl alcohol were placed in a flask, and the contents heated on a water bath at 60-65°. At the close of the reaction the temperature had risen to 70-75°. The vinyl bromide was collected in a receiver immersed in a mixture of snow and salt, washed with glacial acetic acid and dried over calcium chloride. Yield of product (b.p. 16°) 55 g (63% of theory).

Polymerization of vinyl bromide. 16 g of vinyl bromide and 0.032 g benzoyl peroxide were sealed into an ampulla which was left in a dark place. Polymerization commenced after 2-3 days. After 7-10 days the ampulla was opened.

The yield of polymer was 2-2.5 g; a 100% yield of polymer was obtained under these conditions after standing for two months. Vinyl bromide polymer is a white, friable mass, which decomposes and blackens at 120°.

Solubility of polyvinyl bromide in various solvents. In ethylene dibromide, 2%; in chlorobenzene, 1%, in dioxan in the cold, 0.05%; in dioxan on heating, 0.6%; in ethylene dichloride, 0.5%; in benzyl chloride, 0.2%; in ethyl bromide, 0.3%; in carbon bisulfide and nitrobenzene, slightly soluble; in alcohol, ether, and acetone, insoluble.

Bromine determination (by fusion with sodium in a sealed tube for 1 hour at 320° [12]):

0.1175 g substance: 14.27 ml 0.1 $\underline{N}$ AgNO$_3$
Found %: Br 72.53.
C$_2$H$_3$Br. Computed %: Br 74.74.

Saponification of polyvinyl bromide. 3 g polymer and 9 g solid caustic alkali were boiled with 500 ml dioxan for 16 hours. The cooled solution was filtered, and the precipitate, (a light-brown powder) was washed with water until neutral and dried.

2 g of saponification product was isolated. Br content 5.5%.

In conclusion, thanks are expressed to Academician A.N.Nesmeyanov for his interest in the investigation and for valuable advice during preparation of the paper.

SUMMARY

1. Vinyl iodide is shown to be capable of polymerization.

2. A study is made of the properties of 1,2-diiodoethane, which has a strong tendency to break down to iodine and ethylene.

3. The polymerization of vinyl bromide is investigated, and iodine is shown to be an inhibitor of the process.

4. Some properties of polyvinyl bromide are studied.

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ORGANIC INSECTOFUNGICIDES

X. THE SYNTHESIS OF DIALKYL DISULFIDES

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In recent years organic compounds of sulfur have been increasingly attracting the attention of investigators, and they have begun to find application in various fields of the national economy. Many sulfur compounds of the aliphatic series find application, in particular, as insecticides and fungicides in the battle with diseases and pests of plants [1,2,3]. Aliphatic thiocyanates, polysulfides, sulfides, dithiocarbonic acid derivatives, and many others are used as insecticides and fungicides.

With the objective of studying the relation between structure and insecticidal activity, it was considered of interest to synthesize a series of isomeric high-molecular disulfides, since the majority of the compounds of this type have not been studied from this standpoint and have not been described in the literature. Disulfides can also be used for the synthesis of aliphatic sulfonic acids and of various derivatives of sulfenic acids. To the latter group belong, as is well known, allicin and its homologs, which possess fairly high bactericidal activity [4]. We synthesized disulfides by reacting alkyl bromides with sodium disulfide in an aqueous alcoholic medium: $2RBr + Na_2S_2 \rightarrow R-S-S-R + 2NaBr$.

The synthesized disulfides are oily liquids with a straw-yellow color, distilling in vacuum without decomposition. At high temperatures they decompose into olefin and hydrogen sulfide. The majority of the compounds have not been described in the literature.

EXPERIMENTAL

All of the disulfides were prepared in the following manner: 0.15 mole sodium sulfite (crystalline) was dissolved in 45 ml water and heated with continuous stirring with 0.15 g-atom sulfur until the latter was completely dissolved; the resultant solution of sodium disulfide was diluted with 160-ml alcohol, and through a dropping funnel was added an alcoholic solution of the alkyl bromide (0.3 mole). The reaction mixture was refluxed in a flask for several hours with continuous mechanical stirring. The solution was then diluted with water and the disulfide extracted with ether; the ethereal solution was dried with calcium chloride, the ether distilled off, and the disulfide distilled in vacuum.

With increasing molecular weight of the disulfides, and increasing complexity of the molecule due to branching of the hydrocarbon radicals, the disulfides became less stable, and their decomposition was observed both in the process of synthesis and during distillation. Particularly unstable are disulfides containing a tertiary carbon atom linked to sulfur.

It should be noted that the sulfur content of some of the synthesized compounds is rather higher than the calculated values. This is accounted for by the presence of traces of a trisulfide, the separation of which involves great

Prep. No.	Formula	b.p.	d_4^{20}	n_D^{20}	MR_D computed	found	yield %	Sulfur analysis (Carius) weight of substance g	wt. of BaSO4 obtained g	%S found	%S compute
1	CH_3CH_2 \ $CH_3CH_2CH_2CH_2$ / CH-S-S-CH \ CH_2CH_3 / $CH_2CH_2CH_2CH_3$	130-131 at 3 mm	0.9033	1.4865	82.65	83.65	50.1	0.1197 / 0.0945	0.2150 / 0.1719	24.66 / 24.98	24.4
2	CH_3CH_2 \ $(CH_3)_2CHCH_2$ / CH-S-S-CH \ CH_2CH_3 / $CH_2CH(CH_3)_2$	136-142 at 8 mm	0.9027	1.4873	82.65	83.67	40.7	0.1134	0.2101	25.47	24.4
3	$(CH_3)_2CH$ \ $CH_3CH_2CH_2$ / CH-S-S-CH \ $CH(CH_3)_2$ / $CH_2CH_2CH_3$	125 at 1 mm	0.9172	1.4853	82.65	82.06	12	0.1036	0.1826	24.16	24.4
4	CH_3 \ $CH_3(CH_2)_5$ / CH-S-S-CH \ CH_3 / $(CH_2)_5CH_3$	169-171 at 6 mm	0.9010	1.4871	91.87	92.74	37	0.0811 / 0.0829	0.1377 / 0.1415	23.31 / 23.44	22.0
5	$(CH_3)_2CH$ \ $CH_3(CH_2)_3$ / CH-S-S-CH \ $CH(CH_3)_2$ / $(CH_2)_3CH_3$	137-138 at 1 mm	0.9147	1.4880	91.87	91.53	15	0.0936 / 0.1118	0.1487 / 0.1799	21.80 / 22.09	22.0
6	$CH_3CH_2CH_2$ \ $CH_3(CH_2)_5$ / CH-S-S-CH \ $CH_2CH_2CH_3$ / $(CH_2)_5CH_3$	137-139 at 1 mm	0.9003	1.4857	91.87	92.61	29	0.1247	0.2063	22.71	22.0
7	$CH_3(CH_2)_7CH_2$-S-S-$CH_2(CH_2)_7CH_3$	185-193 at 7 mm	0.8772	1.4775	-	-	36	-	-	-	-
8	CH_3CH_2 \ $CH_3(CH_2)_6$ / CH-S-S-CH \ CH_2CH_3 / $(CH_2)_6CH_3$	155 at 2 mm	0.8933	1.4819	101.12	101.66	32	0.0836	0.1243	20.42	20.1
9	$CH_3(CH_2)_3$ \ $CH_3(CH_2)_3$ / CH-S-S-CH \ $(CH_2)_3CH_3$ / $(CH_2)_3CH_3$	175-185 at 6 mm	0.8936	1.4841	101.12	101.76	49	0.1492	0.2226	20.49	20.1
10	$(CH_3)_2CHCH_2CH_2$ \ $CH_3CH_2CH_2$ / CH-S-S-CH \ $CH_2CH_2CH(CH_3)_2$ / $CH_2CH_2CH_3$	185-167 at 7 mm	0.8925	1.4819	101.12	101.75	27	0.1055 / 0.1140	0.1562 / 0.1692	20.27 / 20.38	20.1
11	$(CH_3)_2CHCH_2$ \ $CH_3(CH_2)_3$ / CH-S-S-CH \ $CH_2CH(CH_3)_2$ / $(CH_2)_3CH_3$	143-151 at 1 mm	0.9040	1.4820	101.12	100.47	18	0.1472	0.2226	20.76	20.1
12	$(CH_3)_2CH$ \ $(CH_3)_2CHCH_2CH_2$ / CH-S-S-CH \ $CH(CH_3)_2$ / $CH_2CH_2CH(CH_3)_2$	148-150 at 1 mm	0.9128	1.4923	101.12	101.32	20	0.0942	0.1412	20.58	20.1
13	$(CH_3)_2CHCH_2$ \ $(CH_3)_2CHCH_2$ / CH-S-S-CH \ $CH_2CH(CH_3)_2$ / $CH_2CH(CH_3)_2$	150 at 1 mm	0.8870	1.4795	101.12	101.95	44	0.1246 / 0.0903	0.1808 / 0.1326	19.92 / 20.11	20.1
14	$CH_3(CH_2)_6CH_2$-S-S-$CH_2(CH_2)_6CH_3$	-	0.8907	1.4813	110.36	110.76	77	-	-	-	-
15	$CH_3(CH_2)_6$ \ $CH_3CH_2CH_2$ / CH-S-S-CH \ $(CH_2)_5CH_3$ / $CH_2CH_2CH_3$	-	0.8946	1.4815	110.36	110.33	69	-	-	-	-
16	CH_3 $CH_3CH_2CH_2CH$—C S S—C-$CH_2CH_2CH_2CH_3$ $CH_3CH_2CH_2CH_2$ \ / $CH_2CH_2CH_2CH_3$	-	0.9135	1.4870	110.36	109.03	10	-	-	-	-
17	$(CH_3)_2CHCH_2$ \ $(CH_3)_2CHCH_2CH_2$ / CH S S-CH \ $CH_2CH(CH_3)_2$ / $CH_2CH_2CH(CH_3)_2$	145-150 at 3 mm	0.8908	1.4765	11.36	109.80	10	-	-	-	-
18	$(CH_3)_2CHCH_2CH_2$ \ $(CH_3)_2CHCH_2CH_2$ / CH-S-S-CH \ $CH_2CH_2CH(CH_3)_2$ / $CH_2CH_2CH(CH_3)_2$	-	0.8873	1.4821	119.60	120.30	76	-	-	-	-
19	$(CH_3)_2CHCH_2$ \ $CH_3(CH_2)_6$ / CH-S-S-CH \ $CH_2CH(CH_3)_2$ / $(CH_2)_6CH_3$	175-180 at 1 mm	0.8905	1.4810	119.60	119.70	42	0.1544	0.2032	18.07	17
20	$CH_3(CH_2)_3$ \ $CH_3(CH_2)_5$ / CH-S-S-CH \ $(CH_2)_3CH_3$ / $(CH_2)_5CH_3$	190-192 at 1 mm	0.8810	1.4811	119.60	120.58	64	0.0837 / 0.0643	0.1052 / 0.1072	17.21 / 17.43	17

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difficulties. The compounds prepared and their properties are detailed in the table.

SUMMARY

A series of aliphatic disulfides have been synthesized which have not been described in the literature. It is shown that disulfides with a highly branched carbon skeleton are obtained in low yields by the reaction of alkyl bromides with sodium disulfide. The low yield of these compounds is associated with the presence of side reactions yielding olefins.

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ORGANIC INSECTOFUNGICIDES

XI. SYNTHESIS OF ALKYL SULFONATES WITH AN ISO STRUCTURE
AND THE SURFACE TENSION OF THEIR AQUEOUS SOLUTIONS

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As is well know, the efficiency of various insecticides and fungicides is increased by the addition to the preparations of surface-active substances promoting more uniform distribution of the poisonous chemical over the surface of the plant and its penetration through the trachea and covering of the insect. Surface-active agents are also used for the preparation of a variety of insecticidal emulsions and suspensions. The largest group of substances used in these fields comprises the alkyl, aryl, and alkaryl sulfonates of the alkali metals which are readily accessible and are produced on an adequate scale [1]. It must be pointed out, however, that in the majority of cases the choice of surface active compounds is made by purely empirical methods, and no studies have been made of the relation between structure and surface activity of this type of compound, if we exclude the studies devoted to the properties of alkyl sulfates [2].

In connection with the foregoing observations, we undertook the present investigation on the synthesis and determination of surface tension of aqueous solutions of alkyl sulfonates with an iso structure. The alkyl sulfonates were synthesized by oxidation of the recently described dialkyl sulfides [3] with nitric acid or by their chlorination in an aqueous medium.

The following generalizations may be made on the basis of the determinations of the surface tension of aqueous solutions of alkyl sulfonates: 1. With increasing molecular weight of the sulfonates, the surface tension of its aqueous solution falls; this dependence is also known to be valid for many other classes of compounds. 2. The lowest surface tension is possessed by aqueous-solutions of alkyl sulfonates of normal structure containing a terminal sulfo group. It should be noted, however, that this statement is not applicable to all concentrations of the solutions. At lower concentrations greater activity is manifested by sulfonates of normal structure containing a sulfo group at some distance from the end of the chain. The least active of the investigated compounds were those containing a sulfo group in the middle of the chain. 3. A great influence upon the surface activity of a compound is exerted by the accumulation of methyl groups and their positions relative to the sulfo group.

The second generalization may be explained by the differing degree of adsorption at the surface of compounds of different structures at high and low

Prep. No.	Formula	Mol. Wt.	Surface tension (dynes/cm²) at solution concentration of:				Analysis for Potassium (Carius)			
			1%	0.5%	0.25%	0.1%	Wt. (g)	amount of sulfate of K (Na) obtained (g)	%K (Na) found	%K (Na) computed
1	$CH_3CH_2CH(SO_3K)(CH_2)_3CH_3$	218.3	63.1	66.8	67.9	68.9	0.0838	0.0340	18.21	17.91
2	$CH_3 \big>CHCH_2CH(SO_3K)CH_2CH_3$ (with CH_3)	218.3	54.9	59.5	67.6	69.3	0.0976 / 0.1058	0.0396 / 0.0430	18.20 / 18.24	17.91
3	$CH_3CH(SO_3K)(CH_2)_5CH_3$	232.3	57.7	62.7	65.7	67.6	0.1882	0.0856	26.76 (Ba*)	26.23 (Ba*)
4	$CH_3(CH_2)_2CH(SO_3K)(CH_2)_3CH_3$	232.3	53.6	59.9	66.9	68.0	0.0962 / 0.1430	0.0362 / 0.0524	16.88 / 16.44	16.83
5	$CH_3(CH_2)_7CH_2SO_3K$	246.3	38.8	52.0	58.6	67.1	0.0861 / 0.0974	0.0314 / 0.0354	16.36 / 16.31	15.88
6	$CH_3CH_2CH(SO_3K)(CH_2)_5CH_3$	246.3	40.0	45.1	59.2	65.6	0.0946 / 0.1038	0.0340 / 0.0360	16.13 / 15.56	15.88
7	$CH_3CH_2CH(SO_3Na)(CH_2)_5CH_3$	230.2	37.6	42.8	53.9	62.6	0.1288	0.0424	10.66 (Na)	9.99 (Na)
8	$CH_3(CH_2)_3CH(SO_3K)(CH_2)_3CH_3$	246.3	48.1	55.3	63.1	68.3	0.1374 / 0.0964	0.0486 / 0.0344	15.87 / 16.01	15.88
9	$CH_3 \big>CHCH_2CH_2CH(SO_3K)CH_2CH_2CH_3$ (with CH_3)	246.3	50.2	58.2	64.3	67.7	0.0888	0.0320	16.17	15.88
10	$CH_3 \big>CH(CH_2)_2CH(SO_3Na)(CH_2)_2CH_3$ (with CH_3)	230.2	48.3	55.5	54.9	66.4	0.0984 / 0.1214	0.0316 / 0.0380	10.13 (Na) / 10.40	9.99 (Na)
11	$CH_3 \big>CHCH_2CH(SO_3K)(CH_2)_3CH_3$ (with CH_3)	246.3	47.2	53.6	58.7	67.9	0.1776	0.0398	15.19	15.88
12	$CH_3 \big>CH-CH(SO_3K)(CH_2)_2CH \big< CH_3$ (with CH_3 and CH_3)	246.3	46.6	52.8	56.8	64.7	0.0796	0.0296	16.68	15.88
13	$CH_3 \big>CHCH_2CH(SO_3K)CH_2CH \big< CH_3$ (with CH_3 and CH_3)	246.3	49.3	53.3	60.5	64.8	0.1360 / 0.1044	0.0478 / 0.0376	15.77 / 16.24	15.88
14	$CH_3(CH_2)_8CH_2SO_3K$	260.3	35.5	48.7	57.2	62.3	0.0898 / 0.0884	0.0298 / 0.0294	14.89 / 14.92	15.02
15	$CH_3 \big>CHCH_2CH(SO_3K)(CH_2)_2CH \big< CH_3$ (with CH_3 and CH_3)	260.3	46.6	52.6	63.8	64.6	0.1294 / 0.1288	0.0436 / 0.0444	15.21 / 15.47	15.02
16	$CH_3 \big>CHCH_2CH(SO_3K)(CH_2)_5CH_3$ (with CH_3)	274.4	34.2	41.5	45.8	53.7	0.2070 / 0.2122	0.0646 / 0.0660	14.01 / 14.43	14.21
17	$CH_3(CH_2)_2CH(SO_3K)(CH_2)_5CH_3$	274.4	34.9	39.4	45.4	56.9	-	-	-	-

The barium salt was analyzed. The potassium salt was prepared by treating the aqueous solution of barium salt with an exact equimolar quantity of potassium sulfate. The potassium salt was not isolated in the solid form, and after separating the barium sulfate the aqueous solution was used for surface tension determinations.

concentrations. At low concentrations, compounds containing a sulfo group not at the end of the chain more quickly fill the surface layer, and consequently the surface tension of their aqueous, solutions is rather lower than that of compounds containing a terminal sulfo group. At high concentrations this circumstance has little importance.

EXPERIMENTAL

Alkyl sulfonates of the given structure were synthesized by two routes: 1) by chlorination of dialkyl disulfides in an aqueous medium followed by saponification of the resultant alkyl sulfochloride: and 2) by oxidation of alkyl disulfides with nitric acid (specific gravity 1.4). It was soon decided to abandon the first method since it yields, in addition to the alkyl sulfochlorides, considerable quantities of chlorides, the separation of which is difficult owing to the low stability of the high-molecular sulfochlorides. Most of the alkyl sulfonates were accordingly prepared by oxidation of dialkyl disulfides with nitric acid. Preparation was effected by adding to the disulfides, drop by drop, and with mechanical stirring, the theoretically required amount of nitric acid (sp. gr. 1.4). The reaction proceeds with great violence with evolution of a large amount of oxides of nitrogen, and the reaction mixture darkens. After the addition of the whole of the required amount of nitric acid, the product was heated for an hour on a water bath; after cooling it was neutralized with caustic potash or barium hydrate. The solution of salts was evaporated to dryness on the water bath; in order to remove the sulfones, sulfoxides and resins, the dry salts were washed with ether and the sulfonate separated from the nitrate by extraction with alcohol in which nitrates are insoluble. The sulfonate was purified by recrystallization from alcohol.

It should be noted that sulfonates of alkali metals are extremely hygroscopic and are obtained in the anhydrous state only after prolonged drying over phosphorus pentoxide. Barium sulfonates are converted into potassium or sodium sulfonates by treatment with a carbonate or a sulfate.

With the exception of the sulfonates of normal structure containing the sulfo group at the end of the chain, all of the compounds synthesized by us have not been described in the literature.

The compounds synthesized by us and their properties are listed in the table.

The surface tensions of the aqueous solutions of the alkyl sulfonates were determined by P.A.Rebinder's method.

SUMMARY

A series of alkyl sulfonates which have not been described in the literature were synthesized and the surface tensions of their aqueous solutions of various concentrations determined. It was shown that the magnitude of the surface tension of aqueous solutions of alkyl sulfonates of identical molecular weight and in the same concentrations differ among themselves and depend on the structure of these compounds.

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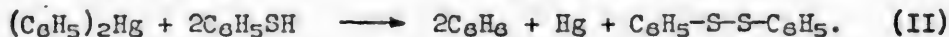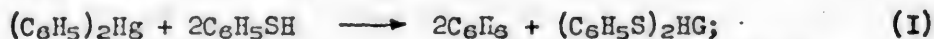Received February 4, 1949.

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REACTIONS OF ORGANO-METALLIC COMPOUNDS WITH THIOPHENOLS

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In a study of the reactions of organo metallic compounds with phenols, we showed that organic compounds of lead, tin, and bismuth form hydrocarbons and phenolates of the metals of varying degrees of stability. In the present paper we continue the study of the reactivity of organo-metallic compounds, using various thiophenols. We have established that organic compounds of mercury, lead, tin, and bismuth enter into reaction with the SH group of thiophenols with formation of hydrocarbons, and disulfides and thiophenolates of the metals.

Diphenyl mercury reacts energetically at 130° with p-thiocresol and with thiophenol with separation of metallic mercury (10-25%), and formation of benzene and of disulfides and thiophenolates of mercury in the form of white crystalline, highly stable compounds:

$$(C_6H_5)_2Hg + 2C_6H_5SH \longrightarrow 2C_6H_6 + (C_6H_5S)_2HG; \qquad (I)$$

$$(C_6H_5)_2Hg + 2C_6H_5SH \longrightarrow 2C_6H_6 + Hg + C_6H_5-S-S-C_6H_5. \qquad (II)$$

The main reaction is (I); rise of temperature and prolongation of heating accelerates reaction (II).

Triphenyl bismuth reacts even at 75-100° with thiophenols, giving benzene and disulfides and golden-yellow thiophenolates of bismuth, or red amorphous products of their partial hydrolysis.

Tetraphenyl lead reacts with thiophenols at 130-150° with formation of benzene and of disulfides and thiophenolates of divalent lead in the form of golden-yellow crystals:

$$(C_6H_5)_4Pb + 4C_6H_5SH \longrightarrow 4C_6H_6 + (C_6H_5S)_2Pb + C_6H_5-S-S-C_6H_5 \qquad (III)$$
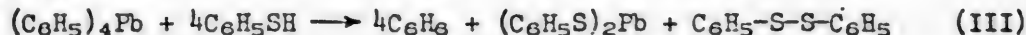
Tetraphenyl tin enters more reluctantly into reaction with thiophenols, only at 150° when benzene and highly viscous yellow liquids are formed. After prolonged standing, druses of colorless acicular crystals separate out. They are the products of partial hydrolysis of the thiophenolates of tin.

EXPERIMENTAL

All of the experiments were performed with heating of the mixture of compounds in sealed glass ampullas in thermostats at precisely regulated temperatures.

1. Diphenyl mercury and thiophenol. Experiments were performed at 130° for 3 hours. 0.4 g diphenyl mercury was reacted with 0.3 thiophenol; separation of metallic mercury (0.0601 g, or 26.55%) and formation of benzene was observed. After treating the reaction mixture with alcohol, separation was effected from the alcoholic solution of colorless crystals of diphenyl disulfide $(C_6H_5S)_2$, with m.p. 59-60° (mixed m.p. determination gave 60°). The residue was dissolved

in benzene and after 2 recrystallizations 0.19 g of white crystalline mercury thiophenolate was obtained. M.p. 150-151°.

$$0.0544 \text{ g substance: } 2.605 \text{ ml } 0.1 \text{ N NH}_4\text{CNS.}$$
$$\text{Found \%: Hg } 47.87.$$
$$(\text{C}_6\text{H}_5\text{S})_2\text{Hg. Computed \%: Hg } 47.92.$$

2. Diphenyl mercury and p-thiocresol. Experiments were performed at 130° for 2-4 hours, using 0.4 g diphenyl mercury and 0.3 g p-thiocresol. Metallic mercury (up to 10%) separated out and benzene was formed. After treatment with ether and alcohol, the main bulk was dissolved in hot benzene. Two recrystallizations yielded 0.2 g colorless crystals, m.p. 158-160°.

$$0.0528 \text{ g substance: } 2.36 \text{ ml } 0.1 \text{ N NH}_4\text{CNS.}$$
$$\text{Found \%: Hg } 44.70.$$
$$(\text{CH}_3\text{C}_6\text{H}_4\text{S})_2\text{Hg. Computed \%: Hg } 44.91.$$

The preparation of the thiophenolates are extremely stable and decompose very slightly on boiling for a long time with an alcoholic solution of HCl with formation of thiophenols and HgCl_2.

3. Triphenyl bismuth and thiophenol. Experiments were carried out at 75-130° for 1-3 hours, using 0.3 g triphenyl bismuth and 0.3 g thiophenol. The reaction mass had a dark-green color. Treatment with solvents resulted in separation from the benzene solution of 0.22 g golden-yellow crystals which did not melt at 250°.

$$0.1046 \text{ g substance: } 0.0567 \text{ g BiPO}_4.$$
$$\text{Found \%: Bi } 37.26.$$
$$(\text{C}_6\text{H}_5\text{S})_3\text{Bi. Computed \%: Bi } 37.12.$$

4. Triphenyl bismuth and p-thiocresol. Experiments were carried out at 75--130° and 1-3 hours with 0.3 g each triphenyl bismuth and p-thiocresol. Treatment with solvents was followed by separation from benzene solution of 0.22 g of a brigh-red amorphous mass, m.p. 252-260° with decomposition.

$$0.0884 \text{ g substance: } 0.0781 \text{ g BiPO}_4.$$
$$\text{Found \%: Bi } 60.74.$$
$$(\text{CH}_3\text{C}_6\text{H}_4\text{S})\text{BiO: Computed \%: Bi } 60.05.$$

5. Tetraphenyl lead and thiophenol. Experiments were performed at 130° for 6 hours and at 150° for 3-6 hours with 0.3 g each of tetraphenyl lead and thiophenol. The reaction mass had a greenish-yellow color. Benzene was detected. Treatment with solvents gave a residue of 0.21 g greenish-yellow crystals, m.p. 195-196°.

$$0.0962 \text{ g substance: } 0.0681 \text{ g PbSO}_4.$$
$$\text{Found \%: Pb } 48.36.$$
$$(\text{C}_6\text{H}_5\text{S})_2\text{Pb. Computed \%: Pb } 48.70.$$

From alcoholic solution 0.12 g of colorless crystals of diphenyl disulfide was isolated with m.p. 58-60° (mixed sample 60°).

6. Tetraphenyl lead an p-thiocresol. Experiments were performed at 130° for 6 hours and at 150° for 3-6 hours with 0.3 g of tetraphenyl lead and 0.3 g p-thiocresol, and gave a greenish-yellow reaction mass. After treatment with solvents a residue of 0.25 g greenish-yellow crystals was obtained with m.p. 202-203°.

$$0.0792 \text{ g substance: } 0.0534 \text{ g PbSO}_4.$$
$$\text{Found \%: Pb } 46.08.$$
$$(\text{CH}_3\text{C}_6\text{H}_4\text{S})_2\text{Pb. Computed \%: Pb } 45.69.$$

7. Tetraphenyl tin and thiophenol. 150° for 6 hours, using 0.5 g tin compound and 0.3 g thiophenol. The reaction mass was a transparent liquid. Benzene

was detected. The heavy, thick transparent liquid, on standing, slowly deposited several druses of colorless needles with m.p. 72-79°.

$$0.0590 \text{ g substance: } 0.0182 \text{ g } SnO_2.$$
$$\text{Found \%: Sn 24.31.}$$
$$(C_6H_5S)_3SnOH. \text{ Computed \%: Sn 25.70.}$$
$$(C_6H_5S)_4Sn. \text{ Computed \%: Sn 21.44.}$$

8. Tetraphenyl tin and p-thiocresol. 150° 6 hours, 0.5 g tin compound and 0.3 g p-thiocresol. Reaction mixture consisted of colorless crystals and much transparent liquid. Benzene detected. After treatment with ether, 0.21 g colorless needles was separated from the ethereal solution. M.p. 92-99°.

$$0.1354 \text{ g substance: } 0.0504 \text{ g } SnO_2.$$
$$\text{Found \%: Sn 29.14.}$$
$$(CH_3C_6H_4S)_2Sn(OH)_2. \text{ Computed \%: Sn 29.82.}$$

SUMMARY

1. It is shown that phenyl derivatives of mercury, lead, tin, and bismuth enter into reaction with the SH group of thiophenols with formation of benzene and thiophenolates of the metals.

2. Triphenyl bismuth reacts the most readily with thiophenols, and tetraphenyl tin enters the least readily into reaction. The order of reactivity is Bi > Hg > Pb > Sn.

MERCURATION OF PHENOLS VIII.

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In the course of recent years the author of the present paper and his co-workers have made an exhaustive study of the mercuration of phenols by organic compounds of mercury. In the first studies [1] it was shown that diphenyl mercury very easily mercurates phenols with formation of mono-, di- and trimercury derivatives. Later it was shown that the ability to mercurate phenols according to the general equation:

$$R_2Hg + R'C_6H_4OH \longrightarrow RH + RHgC_6H_3{\overset{R'}{\underset{OH,}{}}} \qquad (I)$$
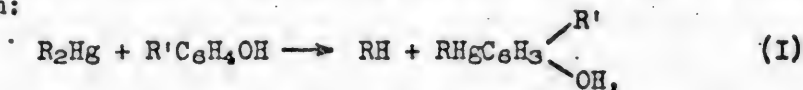
is possessed not only by diphenyl mercury but also by other aryl derivatives of mercury of the general formula R_2Hg (dinaphthyl mercury [1], ditolyl mercury [2]), as well as by alkyl derivatives (diethyl mercury [3], diamyl mercury [4]). In a study of the mercuration of phenols by means of dibenzyl mercury [5] it was found that formation occurs, under the experimental conditions at 100°, of resins, dibenzyl and metallic mercury, so that it appeared that dibenzyl mercury did not behave in the same manner as other R_2Hg compounds.

The author succeeded in demonstrating that, under milder reaction conditions (at 75-80°), dibenzyl mercury forms monomercurated derivatives of phenols which with rising temperature decompose with separation of metallic mercury. The anomalous behavior of dibenzyl mercury in the mercuration of phenols was thus accounted for by the instability of the resultant monomercurated derivatives.

The author also showed that mercuration of phenols may be effected not only by mercury compounds of the R_2Hg type, but also by compounds of the type of $RHgCA$: (for example, phenyl mercuric acetate), when both mono- and dimercurated derivatives of phenols are formed:

$$C_6H_5HgOAc + RC_6H_4OH \longrightarrow HOAc + C_6H_5HgC_6H_3(OH)R. \qquad (II)$$
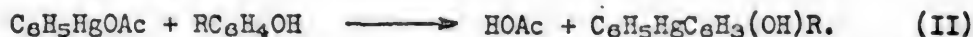
The reaction is accompanied by the separation of free acid (acetic). It should be noted that the velocity of mercuration with C_6H_5HgOAc is lower than with $(C_6H_5)_2Hg$.

In the first communications [1] evidence was adduced for the influence of substituted groups in the phenols on the velocity of mercuration. This investigation has now been continued and a series of new derivatives of diphenyl mercury and substituted phenols has been obtained.

EXPERIMENTAL

All of the experiments were carried out under the conditions described in the preceding communications [1,2,3].

1. Dibenzyl mercury and p-nitrophenol. Heating of 0.2 g dibenzyl mercury and 0.1 g p-nitrophenol at 75° for 2 hours led to the separation of a small quantity of metallic mercury (0.0224 g, or 21.3%) and to the formation of a pinkish, crystalline mass. After elimination of unreacted nitrophenol by treatment with alcohol, the residue was dissolved in benzene. 0.09 g crystalline compound with m.p. 95-97° was obtained.

$$0.0560 \text{ g substance: } 2.625 \text{ ml } 0.1 \underline{N} \text{ NH}_4\text{CNS.}$$
Found %: Hg 46.88.
$C_6H_5CH_2HgC_6H_3(OH)(NO_2)$. Computed %: Hg 46.69.

The product readily splits up on treatment with alcoholic HCl, yielding p-nitrophenol (m.p. 112-114°, mixed sample 114°) and benzyl mercuric chloride (m.p. 102-104°, mixed sample 104°) according to the equation:

$$C_6H_5CH_2HgC_6H_3(OH)(NO_2) + HCl \longrightarrow C_6H_5CH_2HgCl + C_6H_4(OH)(NO_2).$$

2. Reaction of diphenyl mercury and phenyl mercuric acetate with phenols of the first group in the absence of solvents.

The experimental results are summarized in the table.

1) The velocity of reaction with phenols of Group I is greater with diphenylmercury than with phenyl mercuric acetate.

2) The velocities of reaction of cresols with diphenyl mercury are in the order:
$\underline{n}(58.7) > \underline{o}(50.3) > \underline{m}(17.9)$;

3) Substitution in phenols of the benzene ring by the cyclohexane ring lowers the reaction velocity from 48% in the case of thymol to 4.9% in the case of menthol.

Reaction of Diphenyl Mercury and Phenyl Mercuric Acetate with Phenols of Group I in the Absence of Solvents

Expt. No.	Organic mercury compounds	Phenols	Temp.	Amount of mercury separated	
				g	%
1	$(C_6H_5)_2$Hg...	Pyrogallol	130°	0.1275	75.0
2	C_6H_5Hg OAc..	Pyrogallol	130°	0.1161	64.9
3	(C_6H_5)Hg....	Pyrogallol	100	0.0838	49.3
4	C_6H_5HG OAc..	Pyrogallol	100	0.0752	42.2
5	$(C_6H_5)_2$Hg...	Hydroquinone	130	0.1110	65.3
6	C_6H_5Hg OAc..	Hydroquinone	130	0.0946	52.93
7	$(C_6H_5)_2$Hg...	Resorcinol	130	0.1125	66.15
8	C_6H_5Hg OAc..	Resorcinol	130	0.0808	45.3
9	$(C_6H_5)_2$Hg...	p-Cresol	130	0.0998	58.7
10	C_6H_5Hg OAc..	p-Cresol	130	0.0300	17.0
11		m-Cresol	130	0.0315	17.95
12		o-Cresol	130	0.0855	50.33
13	$(C_6H_5)_2$Hg	Metol	130	0.1176	69.20
14		Thymol	130	0.0822	48.35
15		Menthol	130	0.0084	4.94

Note: The amounts of diphenyl mercury and phenyl mercuric acetate were 0.3 g; amount of phenols 0.3 g; duration of heating, 3 hours.

3. Reaction of diphenyl mercury and phenyl mercuric acetate with phenols of Group II.

In all the experiments 0.3 g mercury compound and 0.3 g phenol were heated in sealed glass ampullas in the absence of solvents.

1) Diphenyl mercury and bromohydroquinone. Heating at 130° for 3 hours. After treatment with solvents there was obtained a residue of 0.12 g of a colorless crystalline, infusible and insoluble substance.

$$0.060 \text{ g substance: } 3.24 \text{ ml } 0.1 \underline{N} \text{ NH}_4\text{CNS.}$$
Found %: Hg 54.00.
$(C_6H_5Hg)_2C_6H_3(OH)_2Br$. Computed %: Hg 54.05.

2) Diphenyl mercury and p-chlorophenol. Heating at 100° for 3 hours. Treatment with alcohol was followed by separation from the alcoholic solution of 0.13 g

of white needles of the monomercurated derivative with m.p. 152-154°.

<div align="center">

0.065 g substance: 3.14 ml 0.1 N NH$_4$CNS.
Found %: Hg 48.31.
C$_6$H$_5$HgC$_6$H$_3$(OH)Cl. Computed %: Hg 49.52.

</div>

Heating for 3 hours at 130° led to formation of traces of metallic mercury. The main bulk consisted of dimercurated derivative which separated in the form of a light-yellow, insoluble and infusible product (0.32 g).

<div align="center">

0.055 g substance: 3.18 ml 0.1 N NH$_4$CNS.
Found %: Hg 57.82.
(C$_6$H$_5$Hg)$_2$C$_6$H$_2$(OH)Cl. Computed %: Hg 58.86.

</div>

3) Diphenyl mercury and 2,4-dichlorophenol. At 100° after 3 hours there was formed 0.15 g of finely crystalline monomercurated derivative, soluble in alcohol, with m.p. 139-140°.

<div align="center">

0.062 g substance: 2.80 ml 0.1 N NH$_4$CNS.
Found %: Hg 45.16.
C$_6$H$_5$HgC$_6$H$_2$(OH)Cl$_2$. Computed %: Hg 45.63.

</div>

At 130° after 3 hours only the dimercurated derivative (0.18 g) was obtained in the form of a colorless, insoluble, and infusible product.

<div align="center">

0.055 g substance: 3.05 ml 0.1 N NH$_4$CNS.
Found %: Hg 55.45.
(C$_6$H$_5$Hg)$_2$C$_6$H(OH)Cl$_2$. Computed %: Hg 56.02.

</div>

4) Phenyl mercuric acetate and 2,4-dichlorophenol. Heating at 130° for 3 hours. Free acetic acid was detected. Treatment with solvents was followed by separation of 0.08 g of a colorless, insoluble, and infusible derivative.

<div align="center">

0.051 g substance: 2.85 ml 0.1 N NH$_4$CNS.
Found %: Hg 55.85.
(C$_6$H$_5$Hg)$_2$C$_6$H(OH)Cl$_2$. Computed %: Hg 56.02.

</div>

5) Diphenyl mercury and 2,4,6-trichlorophenol. Heating at 100°, 3 hours. In working up the reaction mass, 0.22 g of monomercurated derivative was isolated from alcoholic solution in the form of colorless needles, m.p. 175-178°.

<div align="center">

0.052 g substance: 2.16 ml 0.1 N NH$_4$CNS.
Found %: Hg 41.54.
C$_6$H$_5$HgC$_6$H(OH)Cl$_3$. Computed %: Hg 42.31.

</div>

Heating for 3 hours at 130° led to formation of the dimercurated derivative (0.2 g) in the form of a colorless, insoluble and infusible crystalline substance.

<div align="center">

0.0992 g substance: 5.23 ml 0.1 N NH$_4$CNS.
Found %: Hg 52.72.
(C$_6$H$_5$Hg)$_2$C$_6$(OH)Cl$_3$. Computed %: Hg 53.44.

</div>

6) Phenyl mercuric acetate and 2,4,6-trichlorophenol. Heating at 100° for 3 hours. Treatment of the reaction mixture with alcohol yielded 0.08 g monomercurated derivative with m.p. 175-177°.

<div align="center">

0.0480 g substance: 2.01 ml 0.1 N NH$_4$CNS.
Found %: Hg 41.87.
C$_6$H$_5$HgC$_6$H(OH)Cl$_3$. Computed %: Hg 42.31.

</div>

Heating at 130° for 3 hours gave 0.12 g dimercurated derivative in the form of an insoluble, infusible crystalline mass.

<div align="center">

0.0601 g substance: 3.17 ml 0.1 N NH$_4$CNS.
Found %: Hg 52.75.
(C$_6$H$_5$Hg)$_2$C$_6$(OH)Cl$_3$. Computed %: Hg 53.44.

</div>

7) Phenyl mercuric acetate and p-nitrophenol. Heating at 130° for 3 hours caused separation of metallic mercury (10%) and formation of dimercurated derivative in the form of a yellow crystalline, insoluble and infusible product.

$$0.0548 \text{ g substance: } 3.19 \text{ ml } 0.1 \text{ N } NH_4CNS.$$
$$\text{Found \%: Hg } 58.13.$$
$$(C_6H_5Hg)_2C_6H_2(OH)NO_2. \text{ Computed \%: Hg } 57.96.$$

8) Diphenyl mercury and 2,4-dinitrophenol. Heating at 100° for 3 hours. Treatment with alcohol yielded, from the solution, 0.17 g bright-red crystals of monomercurated derivative with m.p. 144-148°.

$$0.1 \text{ g substance: } 4.33 \text{ ml } 0.1 \text{ N } NH_4CNS.$$
$$\text{Found \%: Hg } 43.30.$$
$$C_6H_5HgC_6H_2(OH)(NO_2)_2. \text{ Computed \%: Hg } 43.55.$$

Heating at 130° for 3 hours gave the dimercurated derivative (0.19 g) in the form of a bright-yellow crystalline, insoluble and infusible product.

$$0.0508 \text{ g substance: } 2.78 \text{ ml } 0.1 \text{ N } NH_4CNS.$$
$$\text{Found \%: Hg } 54.14.$$
$$(C_6H_5Hg)_2C_6H(OH)(NO_2)_2. \text{ Computed \%: Hg } 54.42.$$

9) Diphenyl mercury and 2,4,6-trinitrophenol. Heating at 100° for 3 hours gave:

a) Monomercurated derivative (0.86 g) separating from alcohol as yellow crystals melting at 157° with decomposition:

$$0.0567 \text{ g substance: } 2.28 \text{ ml } 0.1 \text{ N } NH_4CNS.$$
$$\text{Found \%: Hg } 39.58.$$
$$C_6H_5HgC_6H(OH)(NO_2)_3. \text{ Computed \%: Hg } 39.67.$$

b) Dimercurated derivative (0.14 g); an orange, insoluble and infusible substance:

$$0.0501 \text{ g substance: } 2.55 \text{ ml } 0.1 \text{ N } NH_4CNS.$$
$$\text{Found \%: Hg } 50.90.$$
$$(C_6H_5Hg)_2C_6(OH)(NO_2)_3. \text{ Computed \%: Hg } 51.30.$$

10) Phenyl mercuric acetate and 2,4,6-trinitrophenol. Formation occurred, on heating at 100° for 3 hours, of:

a) Monomercurated derivative (0.17 g); yellow crystals melting at 155-157° (with decomposition).

b) Dimercurated derivative (0.07 g); a yellow, infusible and insoluble substance:

$$0.0488 \text{ g substance: } 2.48 \text{ ml } 0.1 \text{ N } NH_4CNS.$$
$$\text{Found \%: Hg } 50.82.$$
$$(C_6H_5Hg)_2C_6(OH)(NO_2)_3. \text{ Computed \%: Hg } 51.30.$$

11) Diphenyl mercury and resorcinol. Heating at 100° for 3 hours gave 0.05 g of dimercurated derivative; an insoluble and infusible brown substance.

$$0.0420 \text{ g substance: } 2.53 \text{ ml } 0.1 \text{ N } NH_4CNS.$$
$$\text{Found \%: Hg } 60.23.$$
$$(C_6H_5Hg)_2C_6H_2(OH)_2. \text{ Computed \%: Hg } 60.49.$$

12) Diphenyl mercury and p-cresol. Heating at 100° for 3 hours. Treatment with alcohol was followed by separation of 0.24 g light-yellow crystals of monomercurated derivative with m.p. 135-138°.

$$0.0942 \text{ g substance: } 4.90 \text{ ml } 0.1 \text{ N } NH_4CNS.$$
$$\text{Found \%: Hg } 52.02.$$
$$C_6H_5HgC_6H_3(OH)CH_3. \text{ Computed \%: Hg } 52.16.$$

Heating at 130° for 3 hours yielded metallic mercury (up to 60%) and 0.06 g dimercurated derivative in the form of a light-yellow crystalline, insoluble, and infusible substance.

0.0548 g substance: 3.30 ml 0.1 $\underline{N}$ NH$_4$CNS.
Found %: Hg 60.21.
$(C_6H_5Hg)_2C_6H_2(OH)CH_3$. Computed %: Hg 60.68.

13) Phenyl mercuric acetate and p-cresol. Heating at 100° for 3 hours gave 0.12 g monomercurated derivative melting at 135-137°.

0.0622 g substance: 3.24 ml 0.1 $\underline{N}$ NH$_4$CNS.
Found %: Hg 52.09.
$C_6H_5HgC_6H_3(OH)CH_3$. Computed %: Hg 52.16.

14) Diphenyl mercury and m-cresol. Heating at 130° for 3 hours gives:

a) Monomercurated derivative (0.08 g); colorless crystals (from alcohol), m.p. 141-145°.

0.0684 g substance: 4.84 ml 0.1 $\underline{N}$ NH$_4$CNS.
Found %: Hg 52.08.
$C_6H_5HgC_6H_3(OH)CH_3$. Computed %: Hg 52.16.

b) Dimercurated derivative (0.17 g); a colorless crystalline, insoluble and infusible compound.

0.0521 g substance: 3.15 ml 0.1 $\underline{N}$ NH$_4$CNS.
Found %: Hg 60.46.
$(C_6H_5Hg)_2C_6H_2(OH)CH_3$. Computed %: Hg 60.68.

15) Diphenyl mercury and o-cresol. The main product of heating at 100° for 3 hours is the monomercurated derivative (0.17 g) in the form of colorless crystals, readily soluble in alcohol and acetone; m.p. 109-111°.

0.0882 g substance: 4.59 ml 0.1 $\underline{N}$ NH$_4$CNS.
Found %: Hg 52.04.
$C_6H_5HgC_6H_3(OH)CH_3$. Computed %: Hg 52.16.

16) Diphenyl mercury and phenol. Heating at 100° for 3 hours. After treatment of the reaction mixture with solvents, recrystallization from methanol yielded 0.08 g monomercurated derivative in the form of colorless crystals melting at 105-108°.

0.0420 g substance: 2.26 ml 0.1 $\underline{N}$ NH$_4$CNS.
Found %. Hg 53.81.
$C_6H_5HgC_6H_4(OH)$. Computed %: Hg 54.13.

SUMMARY

1. It is shown that the mercuration of phenols can be effected not only with compounds of the type of R$_2$Hg, but also with those of the type of RHgOAc.

2. The R$_2$Hg compounds more readily mercurate phenols than do the corresponding RHgOAc compounds.

3. New derivatives of diphenyl mercury, phenyl mercuric acetate, and various phenols are described.

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THE SULFONATION REACTION

XV. SOME PROPERTIES OF MONOSULFO-SUBSTITUTED NAPHTHALENES

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Dehydration of α- and β-naphthalene sulfonic acids. On crystallization from aqueous solutions containing sulfuric or hydrochloric acid, α-naphthalene sulfonic acid separates with 2 molecules of water [1], while β-naphthalene sulfonic acid separates with 3 molecules of water of crystallization [2]. Various methods have been applied for the preparation of the anhydrous sulfonic acids or their monohydrates. Regnault [3] dried the α-acid in vacuum and obtained the monohydrate with m.p. 85-90°. He did not describe the conditions of drying. Euwes [4] found that the α-acid, dried in vacuum over unslaked lime, had m.p. 87-88°. It was not anhydrous, however. According to Fierz and Weissenbach [1] the dihydrate of the α-acid melts at 90°. The dihydrate loses 1.1 moles of water in 8 days when kept in a desiccator over concentrated sulfuric acid. They reported that it is impossible to remove all of the water from the dihydrate of the α-acid without decomposition. Thus, the anhydrous acid has not hitherto been prepared.

Krafft and Roos [5] prepared the anhydrous β-acid by drying in a vacuum desiccator at 80-85° and 15 mm for 10-12 hours, while in a desiccator at the normal pressure they obtained the monohydrate, but they did not state the drying medium. Euwes [4] reported that after heating for 8 hours at 90° and 20 mm, the acid still contained 3% water. Witt [2] stated that the trihydrate of the β-acid loses 2 moles of water in a desiccator over sulfuric acid or calcium chloride. Drying in a current of dry air at 110° yields the anhydrous β-acid which melts at 90.5-91°.

In the present investigation, anhydrous α- and β-naphthalene sulfonic acids or their monohydrates were prepared mainly by drying in a desiccator over various drying media.

α-Naphthalene sulfonic acid in the form of the dihydrate, dried in a room in an open vessel, still contains a little water, as a rule, over and above 2 moles. This water can be removed by drying over calcium chloride. Over lumps of potassium hydroxide the acid loses one mole of water and changes into the monohydrate. Thus a dihydrate with molecular weight 245.9 (by titration with 0.1 N caustic) was calculated to contain 2.1 moles water; it was dried to constant weight in a calcium chloride desiccator, and then over potassium hydroxide.

    1.4301 g dihydrate: loss in weight over $CaCl_2$ 0.0157 g,

                          calculated for 0.1 mole water   0.0106 g;

                          loss in weight over KOH   0.1025 g,

                          calculated for 1 mole water   0.1045 g.

The dihydrate likewise loses 1 mole water over solid caustic soda and over phosphorus pentoxide. It was noticed, however, that at higher than room temperature over phosphorus pentoxide, the acid can lose 2 moles of water. Thus, the anhydrous α-acid was prepared by drying over phosphorus pentoxide in a desiccator heated in a drying cupboard for about 80 hours at 45-55°.

8.562 g dihydrate: loss in weight over P_2O_5 ....   1.258 g.
                 calculated for 2 moles water........   1.252 g.

The molecular weight of the product was found to be 208.1 (by titration with 0.1 $\underline{N}$ caustic alkali).

With rising temperature and falling pressure the dehydration proceeds considerably faster. The dihydrate loses both of the molecules of water after heating for 4-6 hours at 77° over phosphorus pentoxide at a pressure of 10 mm mercury column.

0.7015 g dihydrate: loss in weight after 4 hours 0.1028 g,
                  calculated for 2 moles water 0.1031 g;
0.9161 g dihydrate: loss in weight after 6 hours 0.1348 g,
                  calculated for 2 moles water 0.1346 g.

The anhydrous α-naphthalene sulfonic acid prepared in this manner melts at 139-140°.

β-Naphthalene sulfonic acid trihydrate loses two moles of water over calcium chloride, as well as over caustic potash, caustic soda, and phosphorus pentoxide. At a higher temperature (40-50° or higher) over phosphorus pentoxide the last mole of water is also driven off and the acid becomes anhydrous. In Table 1 is shown the water content of both of the sulfonic acids over various dehydrating media, and the melting points of the sulfonic acids.

·TABLE 1

Water Contents, over Drying Media, of Naphthalene Monosulfonic Acids and Their Melting Points

	In air	Over calcium chloride	Over solid NaOH, KOH, and P_2O_5	Over P_2O_5 at 25-77°
α-Acid........	2 moles	2 moles	1 mole	Anhydrous
Melting point.	90°	–	87-88°	139-140°
β-acid	3 moles	1 mole	1 mole	Anhydrous
Melting point.	83°	124°	–	90.5-91°

Solubility of α- and β-naphthalene sulfonic acids and their salts.   In connection with the problems of purification of the α- and β-sulfonic acids by crystellization from hydrochloric acid and with the problems of the separation of the sodium salts of the α- and β-acids and their isolation from their aqueous solutions, a series of determinations were made of the solubility of the α- and β-sulfonic acids in hydrochloric acid and of their sodium salts in water and in aqueous solutions of sodium chloride and sodium sulfate.

The literature contains a series of determinations of the solubility of β-naphthalene sulfonic acid in hydrochloric acid at 30°, [6], as well as of the solubility of the sodium salt of the β-acid in water and in sodium chloride solutions at temperatures of 15-20° to 66° [7]. The solubility of the sodium salt of the α-acid in water and in sodium chloride solutions has not previously been measured.
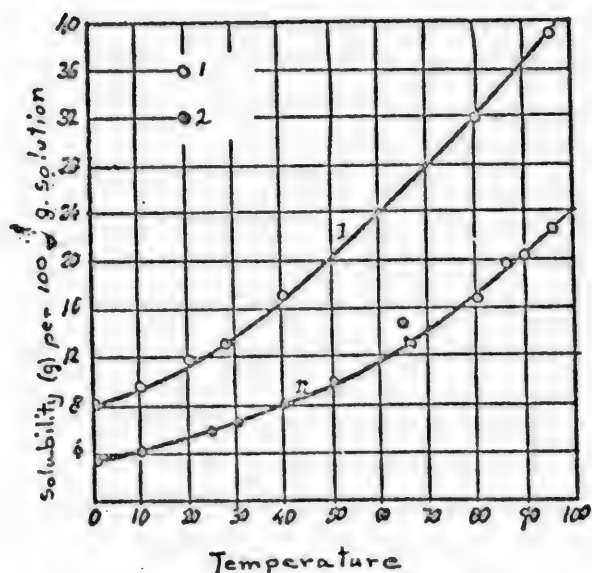
In the determinations described below, the solubility was found of the α- and β-acids in 20% hydrochloric acid at 0° as well as of the sodium salt of the α-acid in water at various températures in the range of 0 to 96°, and in solutions of sodium chloride and sodium sulfate. The solubility in water of the sodium salt of the β-acid was determined at temperatures below 25° and above 65°, since the data of 25 to 65° are given in the literature [7].

The sodium salt of the α-acid has rarely been described in the literature. Fierz-David merely mentions [8] that the salt contains 1/2 mole water which is not driven off by heating on the water bath or by keeping over calcium chloride or 98% sulfuric acid. The anhydrous salt may be obtained by drying at 130° and higher. Results of determinations of solubility are listed in Tables 2, 3, and 4. In the diagram is plotted the solubility of both salts in water according to our determinations and those of Cooke [7].

TABLE 2

Solubility of α- and β-Naphthalene Sulfonic Acids in 20% HCl at 0°

	Anhydrous acid in 100 g solution (g)
β-Acid	0.22
α-Acid	2.23

TABLE 3

Solubility of the Sodium Salts of α- and β-Naphthalene Sulfonic Acids in Water

Temperature	α-Salt in 100 g solution (g)	β-salt in 100 g solution (g)
0°	8.0	3.2
10	9.4	4.1
20	11.7	—
28	12.9	—
40	17.1	—
66	—	13.1
80	31.8	16.8
86	—	19.6
90	—	20.4
96	38.9	22.5

TABLE 4

Solubility of the Sodium Salt of α-Naphthalene Sulfonic Acid in Sodium Chloride Solutions

Temperature	NaCl in 100 g solution, g	α-Salt in 100 g solution, g
0°	24	0.04
0	20	0.07
0	15	0.33
26	15	0.47
30	26	0.13

I) α-Salt; II) β-Salt; 1) Our values; 2) Cooke's values.

The solubility determinations show that the solubility of the sodium salt of the β-acid at all temperatures below 96° does not exceed 22.5%, whereas that of the sodium salt of the α-acid reaches 39%. If we compare these figures with the solubility of sodium chloride and sodium sulfate, it would appear that the solubility of the β-isomer is always less than the solubility of sodium chloride and sulfate, whereas the solubility of the α-isomer exceeds the solubility of sodium chloride and sulfate at temperatures above 68 and 75°. The sodium salt of

the β-acid is almost completely salted out in concentrated solutions of sodium chloride and sulfate at temperatures of 25 to 65° [7]. The sodium salt of the α-acid is only partially salted out by sodium sulfate at 99°. Thus, it was found that 100 g solution saturated with both α-salt and sodium sulfate contains 21.3 g sodium sulfate and 10.7 g salt of α-acid.

EXPERIMENTAL

Dehydration of α-naphthalene sulfonic acid at high temperature in vacuum was effected in the following manner. Into a tube with a diameter of 4 cm were introduced phosphorus pentoxide and a cross piece of glass rod with legs. On the cross piece was fixed a tray containing the dihydrate of the α-acid. The tube was closed with a cork fitted with a thermometer and placed in an Eykman apparatus [9] in which alcohol was boiled. The tube was evacuated at the same time with the aid of a water jet pump.

For the purpose of determining the melting point of the anhydrous α-acid, its dihydrate was dehydrated in exactly the same way in a capillary for 8 hours, instead of the 4 hours required for dehydration in the tray.

Solubility determinations were carried out in a Pawlewski apparatus [10] equipped with a stirrer and stopper. Sodium sulfate was determined gravimetrically. Determination of the solubility of the sodium salt of the α-acid in sodium chloride solutions was effected in the following manner: An exactly weighed small amount of the α-salt was dissolved in 100 g water and to the solution was added a definite amount of sodium chloride. After standing for 6 hours, the separated portion of the α-salt was filtered off and the amount of sodium chloride in the dried residue was determined by the Volhard method.

SUMMARY

1. Determinations were made of the content of water of crystallization in α- and β-naphthalene sulfonic acids over various drying agents.

2. Anhydrous α-naphthalene sulfonic acid has been prepared for the first time and its melting point determined (139-140°).

3. Determinations were made of the solubility of α- and β-naphthalene sulfonic acids in 20% hydrochloric acid at 0°.

4. The solubility was determined of the sodium salt of the α-acid in water at various temperatures and in solutions of sodium chloride and sodium sulfate.

5. Determinations were made of the solubility of the sodium salt of the β-acid in water at various temperatures.

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SPECTROPHOTOMETRY OF BIURET COMPLEXES

AS A METHOD OF INVESTIGATION OF PROTEINS

IX. SPECTROPHOTOMETRIC STUDY OF THE BIURET COMPLEXES OF POLYPEPTIDES AND PROTEIN WITH NICKEL AND COBALT

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A spectrophotometric study of the biuret complexes of polypeptides and proteins with copper salts [1] led to interesting conclusions about the polypeptide portion of the protein molecule. The experimental data obtained at the time support the view that the protein molecule must contain short polypeptide chains — mainly tripeptides and a small proportion of tetrapeptides.

With the objective of obtaining further confirmation of this conclusion, we undertook an investigation in the field of the biuret complexes of polypeptides and proteins with nickel and cobalt.

Very little information has appeared in the literature on the biuret complexes of nickel and cobalt [2]. Apparently, they are mainly complexes of biuret itself. Some workers (Schiff and Traube, for instance) report a course of reaction with nickel and cobalt salts analogous to that with copper salts. Generally speaking, the complexes of polypeptides with nickel and cobalt have not hitherto been investigated. A spectrophotometric study of biuret complexes of nickel and cobalt (both with biuret itself and with peptides and proteins) is now made for the first time.

1. Biuret Complexes of Peptides and Casein with Nickel

We investigated the complexes of glycyl glycine, chloracetylglycyl glycine, diglycyl glycine, chloracetyldiglycyl glycine, triglycyl glycine, tetraglycyl glycine, alanine, tyrosine, and casein.

Solutions of the complexes were prepared in the same manner as for the copper complexes, i.e., by addition to the alkali solution of the peptide, with a definite concentration, of an excess of nickel salt solution. Details are given in the Experimental section.

Nickel biuret complexes of peptides are found to have the following colors: dipeptides — blue; tripeptides — orange; tetra- and pentapeptides — canary yellow; chloracetylglycyl glycine — blue; chloracetyldiglycyl glycine — orange; alanine and tyrosine — pale blue; casein — orange.

The speed of formation of complexes of peptides and protein with nickel is rather lower than that of formation of complexes of peptides and protein with copper. Moreover, for different peptides the rate of formation of the nickel complex is also different. Thus, the most rapid of all is complex formation with tetra- and pentapeptides; the speed is a little lower with dipeptides, and lowest of all in the case of tripeptides. The speed of formation of the Ni-complex of

TABLE 1

Optical Densities ε of Biuret Complexes of Peptides and Protein with Nickel for 0.05 Molar Solutions of Peptides

Prep. No.	Wave-length λ (in mμ)	Glycyl glycine	Chloro-acetyl-glycyl glycine	Diglycyl glycine	Chloro-acetyl-diglycyl glycine	Triglycyl glycine	Tetra-glycyl-glycine	Casein 2% solution	Alanine 0.112 molar	Tyrosine 0.32 molar
1	460	0.053	0.038	–	–	–	2.5	–	0.048	0.012
2	480	0.047	0.029	–	–	–	2.08	–	0.041	0.008
3	500	0.056	0.020	–	–	–	1.42	–	0.048	0.008
4	510	0.057	0.025	–	–	–	1.098	–	0.056	0.110
5	520	0.065	0.022	–	–	–	–	–	–	–
6	540	0.085	0.03	–	–	–	0.44	–	0.112	0.150
7	550	–	–	2.92	–	1.11	0.27	–	0.136	0.180
8	560	0.114	–	1.04	–	0.475	0.196	–	0.162	0.180
9	570	–	–	0.70	0.682	–	0.134	1.43	0.192	0.025
10	580	0.134	0.031	0.42	0.510	0.196	0.100	0.682	0.210	0.026
11	600	–	–	0.266	0.192	0.113	0.064	0.323	0.240	0.038
12	610	0.144	0.03	–	–	–	–	–	0.238	0.034
13	620	–	–	0.194	0.144	0.093	0.044	0.219	0.238	0.04
14	630	0.141	0.036	–	–	–	–	–	–	–
15	640	–	–	0.188	0.104	0.078	0.040	0.177	0.238	0.041
16	660	0.129	0.035	0.219	0.11	0.088	0.034	0.188	0.192	0.043
17	700	–	–	0.294	0.137	0.012	0.046	0.211	0.133	0.026
18	710	0.111	0.033	–	–	–	–	–	–	–
19	730	0.102	0.029	0.408	0.22	0.179	0.076	0.284	0.097	0.027
20	750	0.073	0.028	0.494	0.29	0.223	0.076	0.303	0.068	0.023
Color of complex		Blue	Light Blue	Orange	Orange	Canary yellow	Canary yellow	Orange	Pale blue	Pale green-blue

casein is considerably lower than that of any of the peptide complexes.

A spectrophotometric investigation of solutions of nickel complexes led to the following results. Table 1 gives the values of ε (optical densities for the specified wave lengths).

The data are also plotted in Figure 1.

The first point to be noted is that the curves of this group of complexes (nickel) have no maximum, but a minimum. An exception is the dipeptide complex, which is sharply distinguished both by its color and the character of its absorption. The dipeptide complex has an absorption maximum at 610 mμ. The curve of the tripeptide complex has a minimum at 640 mμ, that of the tetrapeptide at 640 mμ, that of the pentapeptide at 660 mμ, and that of casein at 640 mμ

The distribution of absorption intensities is as follows: the maximum intensity occurs in the case of the tripeptide complex, followed by the tetrapeptide, and then by the pentapeptide. Of greatest interest to us was the great similarity between the casein complex and the tripeptide complex. Both the casein complex and the tripeptide complex have an orange color and the character of the absorption
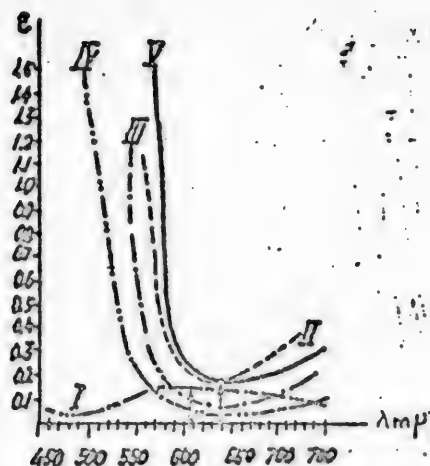
Fig. 1. Spectrophotometric curves of biuret complexes of polypeptides and casein with Ni (0.05 molar solutions of compounds).

I-dipeptide; II-tripeptide; III-tetrapeptide; IV-pentapeptide; V-casein
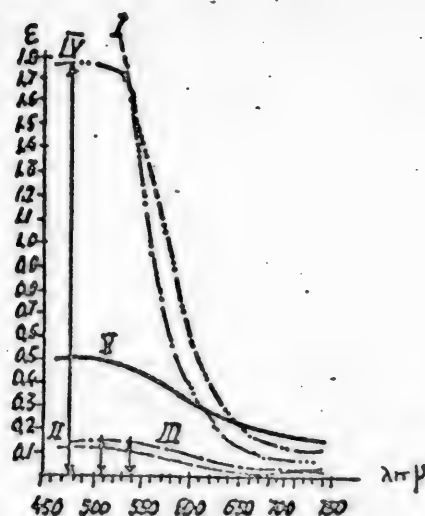

Fig. 2. Spectrophotometric curves of biuret complexes of polypeptides and casein with Co (0.025 molar solutions of compounds).

I-dipeptide; II-tripeptide; III-tetrapeptide; IV-pentapeptide; V-casein, 2%.

in the visible portion is very similar. Consequently, for this group of complexes just as for the copper complexes, we find confirmation of our conclusions. The blue color of the dipeptide complex places this complex in a special category. This fact makes it quite certain that dipeptide cannot be present among the polypeptide chains in protein, for otherwise the color of the protein complex would be green, and the absorption curve of the nickel complex of protein would have a maximum in the 610 mμ region.

2. Biuret Complexes of Peptides and Casein with Cobalt

The peptides investigated were the same as those in the experiments with nickel. The colors of the cobalt complexes differed little from each other; all of them were reddish brown. Amino acids in an alkali medium form with cobalt such weakly colored solutions that doubt arises as to whether complex formation really occurs. Use can be made of this property, however, when it is necessary to distinguish between an amino acid and a dipeptide, the latter forming a strongly colored reddish-brown complex.

Upon standing, the dipeptide complex changes its color to crimson.

Certain observations show that complex formation of peptides with cobalt apparently varies in dependence on the conditions, and is subject to regularities different from those that we encountered in the case of copper complexes. We therefore regard the data in Table 2 and Fig. 2 as having a preliminary character. As shown in Figure 2, the casein curve has the greatest similarity with the tripeptide curve.

3. Biuret Complexes of Nickel and Cobalt with Biuret

The character of the absorption of the biuret complexes of nickel and cobalt with biuret has not been previously investigated.

TABLE 2

Optical Densities ε of the Biuret Complexes of Peptides and Protein with Cobalt for 0.025 Molar Solutions of Peptides

Prep. No.	Wave length, λ, in mμ	Glycyl glycide	Chloracetyl glycyl glycine	Diglycyl glycine	Chloracetyldiglycyl glycine	Triglycyl glycine	Tetraglycyl glycine	Casein 2% solution
1	460	–	0.27	0.114	–	–	1.75	0.453
2	480	–	0.29	0.120	0.67	0.123	1.78	0.499
3	500	–	0.305	0.115	0.604	0.125	1.75	0.492
4	510	–	0.30	0.121	0.602	0.125	1.75	0.489
5	540	–	0.231	0.112	0.50	0.128	1.68	0.452
6	550	1.425	0.210	–	0.44	–	1.55	0.432
7	560	1.2	0.176	0.097	0.39	0.124	1.4	0.415
8	570	–	0.145	–	0.33	–	1.25	0.379
9	580	0.742	0.124	0.077	0.27	0.118	0.109	0.355
10	600	–	0.086	–	0.19	–	0.73	0.333
11	610	0.362	–	0.047	–	0.088	–	–
12	620	\–	0.060	–	0.13	–	0.491	0.31
13	630	0.235	–	0.03	–	0.067	–	–
14	640	–	0.043	–	0.086	–	0.309	0.259
15	660	0.122	0.030	0.019	0.06	0.038	0.214	0.243
16	700	–	0.020	–	0.04	–	0.132	0.195
17	710	0.082	–	0.017	–	0.022	–	–
18	730	0.077	0.019	0.015	0.04	0.025	0.123	0.164
19	750	0.070	0.016	0.018	0.03	0.019	0.099	0.164
Color of complex		Crimson-brown	Reddish-brown	Reddish-brown	Reddish-brown	Reddish-brown	Reddish-brown	Reddish-brown

We have made a spectrophotometric study of the solutions of these complexes. Results are shown in Table 3 and Figure 3. The diagram shows that the curve characterizing the absorption of the nickel complex has no maximum and that it has a minimum at 660 mμ The Co-biuret complex has a maximum of absorption at 480 mμ. At one and the same concentration of biuret, the intensity of absorption is highest with the copper complex, followed by nickel and then by cobalt.

EXPERIMENTAL

The polypeptides were synthesized by Fischer's method [3]. The casein used in the investigation contained 14.13% total nitrogen. The spectrophotometric curves were plotted with the aid of the Kolleman electrospectrophotometer (Model 2).

1. Biuret complexes of peptides with nickel. Solutions of the complexes were prepared in the following manner. A weighed amount of peptide (calculated to give an 0.05 molar concentration) was dissolved in 5 ml water and 2 ml 2 N NaOH. To the solution was added 3.5 ml 0.25 molar solution of $Ni(NO_3)_2$ and the volume of liquid made up to 15 ml with water. After $1\frac{1}{2}$ hours the solution was filtered off from the excess of $Ni(OH)_2$ and examined spectrophotometrically. In some cases, for example in the experiments with tripeptide and tetrapeptide, the solutions were diluted twice for convenience in measurement.

2. Solution of nickel complex of casein. 0.2404 g casein was dissolved in 2 ml of 2 N NaOH and 5 ml water. To the solution was then added 3.5 ml of
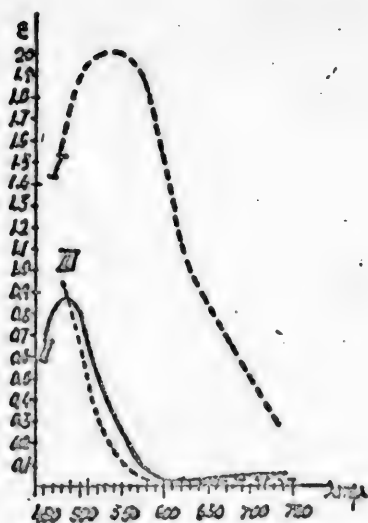
Fig. 3. Spectrophotometric curves of biuret complexes of biuret with Cu, Co, Ni (0.1 molar solutions of biuret).

I-Cu-biuret; II-Co-biuret; III-Ni-biuret

TABLE 3

Optical Densities ε of Biuret Complexes of Nickel and Cobalt (for 0.1 Molar solution of Biuret)

Prep. No.	Wave length in $\lambda m\mu$	Optical density Of Ni complex	Of Co complex
1	460	–	0.673
2	480	0.960	0.870
3	500	0.725	0.840
4	510	0.592	0.755
5	540	–	0.375
6	550	0.128	0.292
7	560	0.080	0.195
8	570	0.054	0.143
9	580	0.033	0.098
10	600	0.014	0.042
11	620	0.012	0.033
12	640	0.012	0.026
13	660	0.011	0.025
14	700	0.018	0.038
15	730	0.030	0.049
16	750	0.038	0.045
Color of complex		Canary-yellow	Reddish-brown

$Ni(NO_3)_2$, and the volume made up to 15 ml with water. After $1\frac{1}{2}$ hours the solution was filtered from the excess of $Ni(OH)_2$.

3. Solution of Ni-biuret complex. 0.1528 g biuret was dissolved in 5 ml water and 1.5 ml 2 $\underline{N}$ NaOH, and to the solution was added 3.5 ml 0.25 molar solution of $Ni(NO_3)_2$, and the volume of liquid made up to 15 ml with water. After $1\frac{1}{2}$ hours the solution was filtered from the excess of $Ni(OH)_2$.

4. Solutions of biuret complexes of peptides and cobalt. The weighed amount of peptide (calculated to form a 0.025 molar solution) was dissolved in 5 ml water and 2 ml 2 $\underline{N}$ NaOH, and to the solution was added 2 ml 0.25 molar $Co(NO_3)_2$, and the volume of liquid made up to 15 ml with water. After $1\frac{1}{2}$ hours the solution was filtered from the excess of $Co(OH)_2$ and subjected to spectrophotometric examination.

5. Solution of biuret complex of casein with cobalt. To 10 ml 2% solution of casein (in 5% NaOH) was added 2 ml 0.25 molar solution of $Co(NO_3)_2$, and the volume made up to 15 ml with water. After $1\frac{1}{2}$ hours the solution was filtered.

6. Solution of Co-biuret complex. 0.1511 g biuret was dissolved in 5 ml water and 1.5 ml 2 $\underline{N}$ NaOH. To the solution was added 2 ml 0.25 molar solution of $Co(NO_3)_2$, and the volume of liquid made up to 15 ml with water. After $1\frac{1}{2}$ hours the solution was filtered from the excess of $Co(OH)_2$.

SUMMARY

1. Biuret complexes of peptides and casein are formed more slowly than the copper complexes; the following colors are developed; dipeptide complex – blue; tripeptide – orange; tetra- and pentapeptides – canary yellow; casein – orange. The spectrophotometric curves do not possess a maximum, with the

exception of the dipeptide complex, and possess a minimum in the 640-660 mµ region.

2. The nickel biuret complex of casein closely resembles the tripeptide complex in color and absorption, and differs from the complexes of longer polypeptide chains such as tetra- and pentapeptides.

3. The marked difference between the dipeptide complex and the complexes of other peptides and casein suggests that the protein molecule does not contain dipeptide chains, for otherwise the color of the nickel complex of protein would be green.

4. Biuret complexes of peptides and casein with cobalt have a reddish-brown color. The chief difference between them resides in the intensity of absorption.

5. The nickel complex of biuret has a canary yellow color, and its absorption curve has a minimum at 660 mµ.

6. The cobalt complex of biuret is reddish-brown and has an absorption maximum at 480 mµ.

7. The intensity of the color of the cobalt biuret complex of the dipeptide is so great in comparison with that of the cobalt complexes of amino acids (such as alanine, glycocoll and tyrosine) that this reaction with cobalt may be recommended as a qualitative one when it is necessary to differentiate between dipeptide and amino acid in solution.

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CYANINE DYES CONTAINING FLUORINE

I. CYANINE DYES FROM DERIVATIVES OF 6-FLUORBENZTHIAZOLE

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Cyanine dyestuffs containing fluorine as substituent have not hitherto been described. It was considered of interest to establish the influence of fluorine upon the properties of cyanine dyestuffs, especially on their light absorption and on their activity as photosensitizers.

We carried out the synthesis of thiocyanines containing an atom of fluorine in the benzthiazole nuclei in position 6. As starting materials we had to synthesize the previously undescribed 2-methyl-6-fluoro- and 2-methylmercapto-6-fluorobenzthiazoles and their quaternary salts.

2-Methyl-6-fluorobenzthiazole was prepared by two methods.

a) 2-Methyl-6-aminobenzthiazole was diazotized in a solution of fluoboric acid. The precipitated diazonium borofluoride was filtered off, dried, mixed with sand (in order to moderate the reaction), and decomposed by heating. The product was distilled in steam. The yield of pure base by this method is aobut 20% calculated on the 2-methyl-6-aminobenzthiazole.

b) The acetyl derivative of p-aminofluorobenzene [1] was converted, by fusion with phosphorus pentasulfide, into p-fluorothioacetanilide, which was then cyclized by Jacobson's reaction (oxidation with potassium ferricyanide) to 2-methyl-6-fluorobenzthiazole. The yield was 15% on the p-fluoroacetanilide.

2-Methyl-6-fluorobenzthiazole, obtained by either of the above methods, forms colorless leaflets melting at 69°.

2-Methylmercapto-6-fluorobenzthiazole was prepared by diazotization of 2-methylmercapto-6-fluorobenzthiazole in HBF_4 solution in the same way as 2-methyl-6-fluorobenzthiazole was prepared. The melting point is 70° and the yield 28% based upon the original amine.

From the quaternary salts of the above two bases, using the usual methods of cyanine dyestuff chemistry, were prepared 11 thiocyanines containing fluorine in position 6. The compounds were symmetrical and asymmetrical monomethine cyanines, as well as merocyanine and a p-dimethylaminostyryl derivative. The structural formulas and absorption maxima of these preparations are presented in Table 1, where are also given, for comparison, the absorption maxima of the corresponding dyes not containing fluorine.
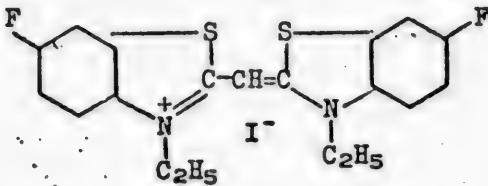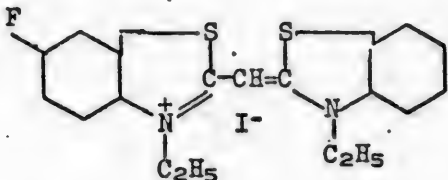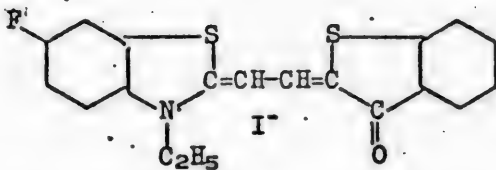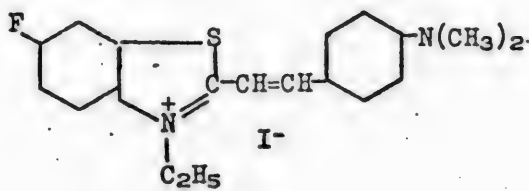
It appears from Table 1 that the absorption maxima of fluorine-substituted thiocyanines scarcely differ from the absorption maxima of the fluorine-free dyes. The molecular extinction of 6,6'-difluorothiocarbocyanine (I) was determined. It,

In ethyl alcohol solution, determined with the Bellingham-Dtanley spectrophotometer.

TABLE 1

No.	Formula of dyestuff	λ_{max} (mμ)	λ_{max} (mμ) for dyestuff not containing fluorine
I		558	558
II		652	651
III		–	755
IV		545	544
V		550	550
VI		578	580
VII		422	422

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TABLE 1 (continuation)

No.	Formula of dyestuff	λ_{max} (mμ)	λ_{max} in mμ for dyestuff not containing fluorine
VIII		422	422
IX		485	487
X		554	556
XI		534	530

too, is close to the extinction of the unsubstituted thiocarbocyanine ($14.5 \cdot 10^4$ and $16.5 \cdot 10^4$, respectively). In other properties, however, the 6-fluorothiocyanines differ from the thiocyanines. They are less soluble in alcohol, have higher melting points, and are decolorized with much greater difficulty by hydrochloric acid than the unsubstituted dyes.

It is interesting to compare the absorption maxima of symmetrical thiocarboxyamines containing different halogen substituents in the 6,6'-position (Table 2).

TABLE 2

Substituent (R)	λ_{max}, mμ
—	558
F	558
Cl	560 (2)
Br	560 (2)
I	571 (3)

EXPERIMENTAL

2-Methyl-6-fluorobenzthiazole. a) To 20 g of 4-fluoroacetanilide in 80 ml dry xylene was added 15 g phosphorus pentasulfide while heating on the water bath and with good stirring. The solution turned yellow and later dark red, and a reddish-brown oil settled to the bottom. After heating for 25 minutes, the xylene layer was decanted off and the residue extracted twice with 80 ml hot xylene on each occasion. On cooling, yellowish crystals of the thioamide came down from

the xylene solution. The mother liquor was concentrated, and the resultant crystals were purified by dissolving in dilute caustic alkali and precipitating with carbon dioxide. In all, 11.2 g thioamide was obtained, or 50.9% of theory. The preparation recrystallized from aqueous alcohol melted at 89-90° (all of the temperatures here given have been corrected):

<div align="center">
Found %: N 8.28.
C_8H_8NSF. Computed %: N 8.23.
</div>

A cooled solution of p-fluorothioacetanilide (10 g in 200 ml 2 $\underline{N}$ sodium hydroxide) was added dropwise with stirring to 200 ml ice-cooled 20% solution of potassium ferricyanide. After mixing of the two solutions, stirring was continued for another 30 minutes. On the following day the yellowish precipitate was filtered off and washed with water to remove the potassium ferrocyanide. It was then dissolved in concentrated hydrochloric acid, decolorized by digestion with animal charcoal, and filtered. Treatment of the solution with caustic alkali led to precipitation of 3.4 g of base, which was recrystallized from petroleum ether. White leaflets with the odor of thiazole. The preparation dissolved easily in acids and organic solvents. Melting point 69°. Yield 3 g, or 30% of theory.

<div align="center">
Found %: N 8.43.
C_8H_6NSF. Computed %: N 8.38.
</div>

b) The following procedure was found to be the best of several variants tested for the substitution of fluorine for the amino group in 2-methyl-6-aminobenzthiazole. 11 g 2-methyl-6-aminobenzthiazole was dissolved in 70 g 40% fluoboric acid (4.5 moles) in a platinum dish, well cooled, and diazotized by dropwise addition of a solution of 5.1 g sodium nitrite in 12 ml water. After standing for 30 minutes on ice and for 15 minutes at room temperature the precipitate of diazonium boron fluoride was filtered off, washed with alcohol and ether, and dried for 24 hours in a vacuum desiccator. Faintly yellow crystals decomposing at 140-142°. Yield 13.3 g, or 75.5% of theory. 13.3 g diazonium boron fluoride was mixed with 40 g dry quartz sand and placed in a round-bottomed flask of 1 liter capacity connected to a well-cooled reflux condenser. The flask was heated until white fumes of BF_3 had ceased to come off, after which 100 ml of 10% sodium carbonate solution were run into the flask and the product was distilled off in steam. The preparation was recrystallized from petroleum ether. Yield 2.2 g, or 26% calculated on the diazonium salt; m.p. 69°.

<div align="center">
Found %: N 8.54.
C_8H_6NSF. Computed %: N 8.38.
</div>

2-Methyl-6-fluorobenzthiazole iodomethylate was prepared by heating 1 g of the base with 0.8 g dimethyl sulfate for 3 hours on a boiling water bath. The product was washed with benzene and precipitated from aqueous solution with potassium iodide. After crystallization from aqueous alcohol the yield was 1.38 g, or 75% of theory; m.p. 264-265° with decomposition.

<div align="center">
Found %: I 41.09.
C_8H_8NSFI. Computed %: I 41.10.
</div>

The iodoethylate of the base was prepared by a similar procedure. The preparation recrystallized from aqueous alcohol melted at 244-245° with decomposition. Yield 78% of theory.

<div align="center">
Found %: I 39.53.
$C_{10}H_{11}NSFI$. Computed %: I 39.32.
</div>

2-Methylmercapto-6-fluorobenzthiazole. 3.5 g 2-methylmercapto-6-aminobenzthiazole [4] was dissolved in 25 g of 40% HBF_4 in a platinum dish, the solution was cooled with ice and diazotized with 1.3 g of solid sodium nitrite. After 30

minutes the yellowish precipitate of the diazonium boron fluoride was filtered off and washed with alcohol and ether. Yield 4.3 g, or 81% of theory; decomposition temperature 156-157°. The product was decomposed by heating with sand and distillation in steam as described above. Crystallization from petroleum ether yielded 1 g of white crystals, m.p. 70°. Yield 34% of theory, calculated on the diazonium salt.

Found %: N 7.01, 7.14.
$C_7H_8NS_2F$. Computed %: N 7.04.

The iodoethylate of the base was prepared by heating for 3 hours on the water bath with diethyl sulfate followed by treatment with potassium iodide. Yield of iodoethylate 71% of theory; m.p. after crystallization from aqueous alcohol 140-141°.

Found %: I 35.89.
$C_{10}H_{11}S_2NFI$. Computed %: I 35.77.

bis-3-Ethyl-6-fluorobenzthiazole-(2)-trimethincyanine iodide (I). 0.5 g of 2-methyl-6-fluorobenzthiazole and 0.5 g of ethyl orthoformate were boiled with 4 ml acetic anhydride for 45 minutes. The dyestuff was recrystallized from alcohol. Green crystals with a metallic luster, m.p. 300-301°, with decomposition. Yield 0.27 g, or 67% of theory. λ_{max} 558 mμ, ε_{max} 14.5·10⁴.

Found %: I 23.92, 23.97.
$C_{21}H_{19}S_2N_2F_2I$. Computed %: I 24.05.

bis-3-Ethyl-6-fluorobenzthiazole-(2)-pentamethincyanine iodide (II). 0.2 g of β-anilinoacrolein anil hydrochloride and 0.5 g 2-methyl-6-fluorobenzthiazole iodoethylate were boiled with 4 ml acetic anhydride and 3 drops triethylamine for 20 minutes. After recrystallization from alcohol the dyestuff melted at 270° with decomposition. Yield 0.21 g, or 50% of theory.

Found %: I 22.67.
$C_{23}H_{21}S_2N_2F_2I$. Computed %: I 22.92.

bis-3-Ethyl-6-fluorobenzthiazole-(2)-heptamethincyanine iodide (III). 0.5 g of 2-methyl-6-fluorobenzthiazole iodoethylate and 0.22 g hydrochloride of the anil anilide of glutaconic aldehyde were dissolved in 5 ml absolute alcohol; to the solution was added a solution of sodium ethylate prepared by dissolving 0.04 g sodium in 1.5 ml absolute alcohol. The mixture was boiled for 2 minutes. The crystals of dyestuff separating on cooling were washed with water, digested with alcohol, and washed with ether. Green crystals, sparingly soluble in alcohol; yield 0.24 g, or 53% of theory. M.p. 243-244° (with decomposition) after recrystallization from alcohol. The alcoholic solution of the dyestuff has an absorption maximum beyond the limits of the visible spectrum.

Found %: I 22.13.
$C_{25}H_{23}S_2N_2F_2I$. Computed %: I 21.90.

bis-3-Ethyl-6-fluorobenzthiazole-(2)-8-methyltrimethincyanine iodide IV). It was prepared from 0.5 g of 2-methyl-6-fluorobenzthiazole iodoethylate and 0.5 g ethyl orthoformate by heating for 45 minutes with 3 ml acetic anhydride and 3 drops of pyridine. After recrystallization from alcohol it formed long, violet needles melting at 307-308° with decomposition. Yield 0.13 g, or 32% of theory.

Found %: I 23.25.
$C_{22}H_{21}S_2N_2F_2I$. Computed %: I 23.43.

bis-3-Ethyl-6-fluorobenzthiazole-(2)-8-ethyltrimethincyanine iodide (V). Condensation of 2-methyl-6-fluorobenzthiazole iodoethylate with ethyl orthoformate in acetic anhydride or pyridine gave a very low yield of dyestuff. The iodomethylate was therefore converted into the chlorethylate by the method of Hamer and Fischer [5]. 0.33 g 2-methyl-6-fluorobenzthiazole chlorethylate and 0.35 g ethyl orthopropionate were boiled with 3 ml acetic anhydride for an hour. The

dyestuff was precipitated from solution with ether, again dissolved in alcohol, and precipitated with potassium iodide. Yield 0.1 g after recrystallization from alcohol, or 27% of theory. M.p. 269-270°, with decomposition.

Found %: I 22.94.
$C_{23}H_{23}S_2N_2F_2I$. Computed %: I 22.84.

3-Ethyl-6-fluorobenzthiazole-(2)-1-ethylquinoline-(2)-trimethincyanine iodide (VI). 0.36 g of 2-methyl-6-fluorobenzthiazole iodoethylate, 0.5 g of 2-acetanilidovinyl quinoline iodoethylate (prepared by Ogata's method [6]), and 0.36 g anhydrous sodium acetate were heated on a boiling water bath with 2 ml acetic anhydride for 15 minutes. Filtration, washing, and crystallization from 75 ml alcohol yielded 0.2 g green crystals with a metallic luster. The yield after a second recrystallization was 0.11 g, or 20% of theory; m.p. 283° with decomposition.

Found %: I 24.99.
$C_{23}H_{22}N_2SFI$. Computed %: I 25.20.

3-Ethyl-6-fluorobenzthiazole-(2)-3-ethylbenzthiazole-(2)-methincyanine iodide (VII). Prepared from 0.25 g 2-methylmercapto-6-fluorobenzthiazole iodoethylate, 0.22 g 2-methylbenzthiazole iodoethylate, and 0.12 g anhydrous sodium acetate by boiling in 4 ml absolute alcohol for an hour. Two crystallizations from alcohol gave lemon-yellow needles, m.p. 294-295°; yield 0.22 g, or 65% of theory.

Found %: I 26.44.
$C_{19}H_{18}S_2N_2FI$. Computed %: I 26.24.

bis-3-Ethyl-6-fluorobenzthiazole-(2)-methincyanine iodide (VIII). Prepared from 0.44 g 2-methylmercapto-6-fluorobenzthiazole iodoethylate and 0.4 g 2-methyl-6-fluorobenzthiazole iodoethylate by the previously described method. Yellow needles melting at 319-320° with decomposition. Yield 0.44 g, or 71% of theory.

Found %: I 25.09.
$C_{19}H_{17}S_2N_2F_2I$. Computed %: I 25.30.

3-Ethyl-6-fluorobenzthiazole-(2)-1-ethylquinoline-(2)-methincyanine iodide (IX). Prepared from 2-methylmercapto-6-fluorobenzthiazole iodoethylate and quinaldine iodoethylate by the previous method. Orange needles, m.p. 285-286° with decomposition. Yield 52% of theory.

Found %: I 26.76.
$C_{21}H_{20}N_2SFI$. Computed %: I 26.57.

2-(3'-Ethyl-6'-fluorobenzthiazolinylidene-2'-ethylidene)-3-oxo-2,3-dihydrothionaphthene (X). 0.15 g of the anil of 3-hydroxythionaphthene-2-aldehyde (prepared from 3-hydroxythionaphthene carboxylic acid and diphenylformamide [7]), 0.19 g 2-methyl-6-fluorobenzthiazole, and 0.2 g anhydrous sodium acetate were heated for 45 minutes with 3 ml absolute alcohol. The precipitated dyestuff was washed and recrystallized from 80 ml alcohol. Red needles melting at 274-275° with decomposition. Yield 0.12 g, or 60% of theory. The preparation exhibits solvatochromy. It has an absorption maximum in alcohol at 554 mμ and in benzene at 530 mμ.

Found %: N 4.09.
$C_{19}H_{14}OS_2NF$. Computed %: N 3.94.

2-p-Dimethylaminostyryl-6-fluorobenzthiazole iodoethylate. 0.5 g 2-methyl-6-fluorobenzthiazole iodoethylate and 0.25 g p-dimethylaminobenzaldehyde were boiled with 5 ml acetic anhydride for 45 minutes. Crystallization from alcohol gave red-violet needles melting at 253-254°, with decomposition. Yield 0.6 g, or 86% of theory.

Found %: I 27.79.
$C_{18}H_{20}N_2SFI$. Computed %: I 27.97.

SUMMARY

1. 2-Methyl-6-fluoro- and 2-methylmercapto-6-fluorobenzthiazoles and their quaternary salts have been synthesized.

2. Eleven thiocyanine dyes containing fluorine as substituent in the 6-position have been prepared.

3. It is shown that the replacement of hydrogen by fluorine in the 6-position of thiocyanines is substantially without influence upon the position of the absorption maximum.

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OBSERVATIONS ON V. N. UFIMTSEV'S PAPER ON

THE BISULFITE COMPOUND OF 1,4 NAPHTHOQUINONE [1]

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In a recently published communication [1], V.N.Ufimtsev made the statement that 1,4-naphthoquinone is capable of reacting with two molecules of potassium (or sodium) bisulfite and that the compound thereby formed is the dipotassium (or disodium) salt of 1,4-dihydroxydihydronaphthalene-1,4-disulfonic acid. In proposing this structure for the compound which he isolated, however, V.N.Ufimtsev did not present in his paper a single experimental fact that could be regarded as convincing evidence of the alleged position of the substituents in the molecule of the substance. Indeed, V.N.Ufimtsev bases his assertion solely on his elementary analysis of the compound that he prepared and on its ability to split off the elements of bisulfite in presence of aqueous solutions of acids and alkalies. In so doing, he loses sight of the fact that this type of behavior toward solutions of acids or alkalies may also occur with bisulfite derivatives of different structure; it follows, therefore, that this type of evidence cannot be regarded as a trustworthy basis either for the structural formula of the substance in question or for the structural formulas of bisulfite compounds of quinones in general.

Furthermore, in the same paper [1] V.N.Ufimtsev states that on repeating the reaction between potassium bisulfite and 1,4-naphthoquinone previously described by us [2], he succeeded in isolating only the dipotassium salt of 1,4-dihydroxydihydronaphthalene-1,4-disulfonic acid. He therefore came to the conclusion that the existence of the bisulfite derivatives of 1,4-naphthoquinone described in one of our earlier papers [2] was questionable.

We deem it desirable to make the following observations on the statements of V.N.Ufimtsev:

1. The experiments described by us on the preparation of bisulfite derivatives of 1,4-naphthoquinone are fully reproducible, as follows from their frequent repetition by us in the course of the long period of our work with these compounds.

2. It is important to note, however, that the bisulfite complex of 1,4-naphthoquinone described by us is an extremely unstable compound which under certain conditions is readily capable of undergoing the further transformations characteristic of this type of bisulfite derivative. The latter, according to our investigations, tend to isomerize in aqueous solutions, the speed of this process being highly dependent upon the temperature. Thus, in a study at various temperatures of the velocity of isomerization of the bisulfite complex of potassium 1,4-naphthoquinone-2-sulfonate (which is considerably more stable than the bisulfite complex of 1,4-naphthoquinone), A.S.Chernyshev established that in a

4.8% aqueous solution the isomerization is completed at 20° in 110 minutes, at 30° in 45 minutes, at 40° in 20 minutes, at 50° in 13 minutes, and at 60° in 7 minutes*. Consequently, the period of isomerization of the given complex is roughly halved for a 10° rise in temperature. In the case of the bisulfite complex of 1,4-naphthoquinone, this isomerization proceeds at a considerably greater velocity and is rapidly completed in aqueous solution even at room temperature. It is precisely for this reason that the bisulfite complex of 1,4-naphthoquinone cannot be purified by recrystallization from water, while its purification by reprecipitation from aqueous solution by alcohol demands great care and must be effected with the utmost speed, just as in the case of preparation of the bisulfite complex itself. We did not emphasize this circumstance with sufficient clarity in our paper [2], and this is possibly the reason for the discrepancy between our results and those of V.N.Ufimtsev.

3. In the light of the factors considered above, the very fact of the existence of, and of the difference in properties between, the two isomeric forms of the bisulfite derivatives of p-naphthoquinones described by us may be most clearly observed in the case not of 1,4-naphthoquinone but of potassium 1,4-naphthoquinone-2-sulfonate, both forms of which (the bisulfite complex and the adduct) can be readily prepared individually (see [2]) and subjected to careful purification.** We have already [2] described the pronounced difference in the chemical behavior of these two forms. These two forms also differ in their physical properties, as for example, in their solubility in water; thus, at 25°, 4.9 g bisulfite complex dissolve in 100 ml water, as compared with 59.0 g adduct of potassium 1,4-naphthoquinone-2-sulfonate.

4. On the basis of the foregoing observations, we reiterate our previous statement of the existence, in the case of certain p-naphthoquinones, of two isomeric forms of the bisulfite derivatives, and we consider the opinion of V.N.Ufimtsev to be unfounded, insofar as he has never put forward decisive evidence of the correctness of his viewpoint respecting the position and character of the substituents in the molecules of these compounds. We may also recall that we recently [3] demonstrated experimentally the error in V.N.Ufimtsev's concepts of the structure of the bisulfite derivative of 2-methyl-1,4-naphthoquinone, these concepts being sharply at variance with the properties studied by us and with the transformations of this bisulfite derivative.

V.N.Ufimtsev's investigations of the structure of bisulfite derivatives of other types of organic molecules will be discussed by us in a separate paper.

SUMMARY

V.N.Ufimtsev's theory of the structure of the product of reaction of 1,4-naphthoquinone with potassium or sodium bisulfite is experimentally unfounded, and his statement about the non-reproducibility of our data relating to this

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* In these experiments the reaction may be considered to be complete when the coupling reaction between the bisulfite complex of potassium 1,4 naphthoquinone-2 sulfonate and a solution of diazotized p-nitraniline, prepared by the usual method [2,3], no longer takes place; it may be noted that this reaction is sensitive to the presence of 0.0005 g complex in 1 ml solution.

** The bisulfite complex of potassium 1,4-naphthoquinone-2-sulfonate is conveniently purified by two reprecipitations from aqueous acetone.

Found %: C 30.43; H 1.81; K 19.70; S 16.16
$C_{10}H_6O_8S_2K_2$. Computed %: C 30.28, H 1.53; K 19.72, S 16.17.

The adduct of potassium 1,4-naphthoquinone-2-sulfonate may be prepared in the pure form by one or two recrystallizations from water.

Found %: C 30.67; H 1.53; K 19.61; S 16.05
$C_{10}H_6O_8S_2K_2$. Computed %: C 30.28, H 1.53; K 19.72, S 16.17.

reaction is inaccurate. Our statement of the existence of two isomeric forms of the bisulfite derivatives of certain p-naphthoquinones has strong experimental support.

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